THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS:

Convention Notice - - - - - - - - - - - - 751

Obituary — L. H. Lincoln - - - - - - - - - - 752

Bureau of Employment - - - - - - - - - - 754

New Members - - - - - - - - - - - - - 754

Estimation of Sulfur in Proteins in General and Leather in Particular. *By* H. Rao - - - - - - - - 755

A Method of Producing Unhairing Liquors from Staple Rayon Industry Wastes. *By* I. Skogestad - - - - 757

Tannin Evaluation of One Hundred Sixty-Three Species of Plants. *By* M. L. Happich, C. W. Beebe and J. S. Rogers - - - - - - - - - - - - 760

Aging Characteristics of Side Leather. *By* W. T. Roddy and J. J. Jansing - - - - - - - - - - 773

Abstracts - - - - - - - - - - - - - - 787

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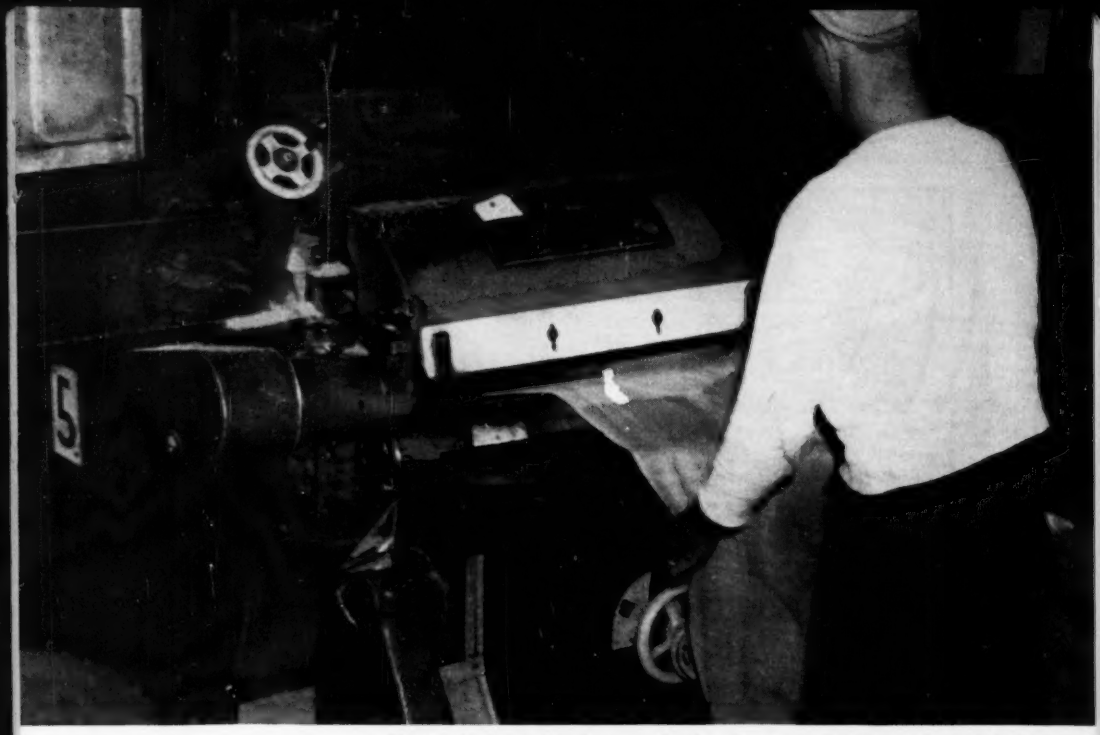

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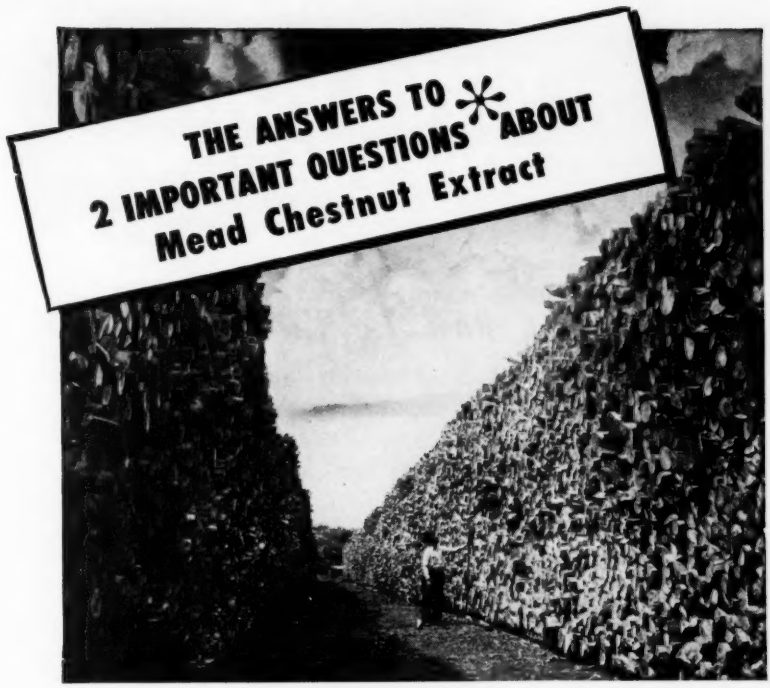

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D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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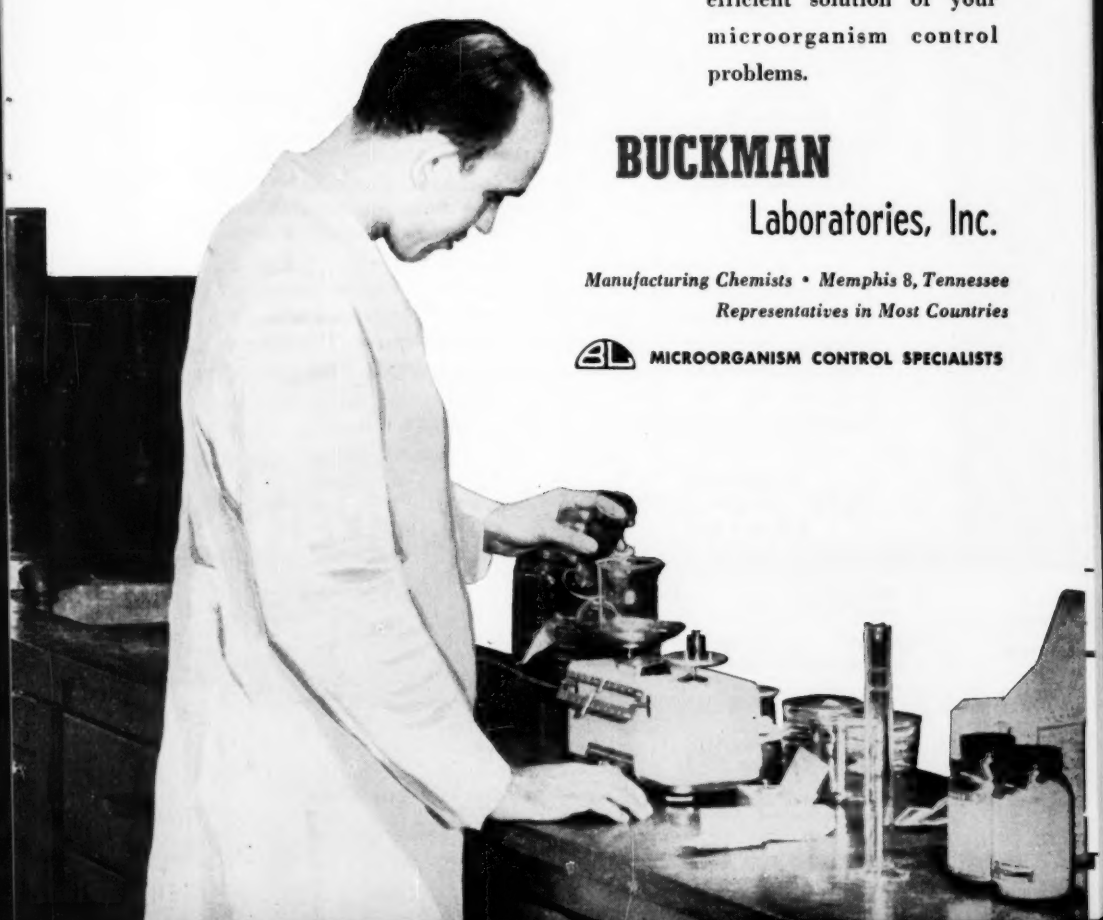

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ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

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Steel drums . . . . 90 and 350 lbs. net

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(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. . . . . 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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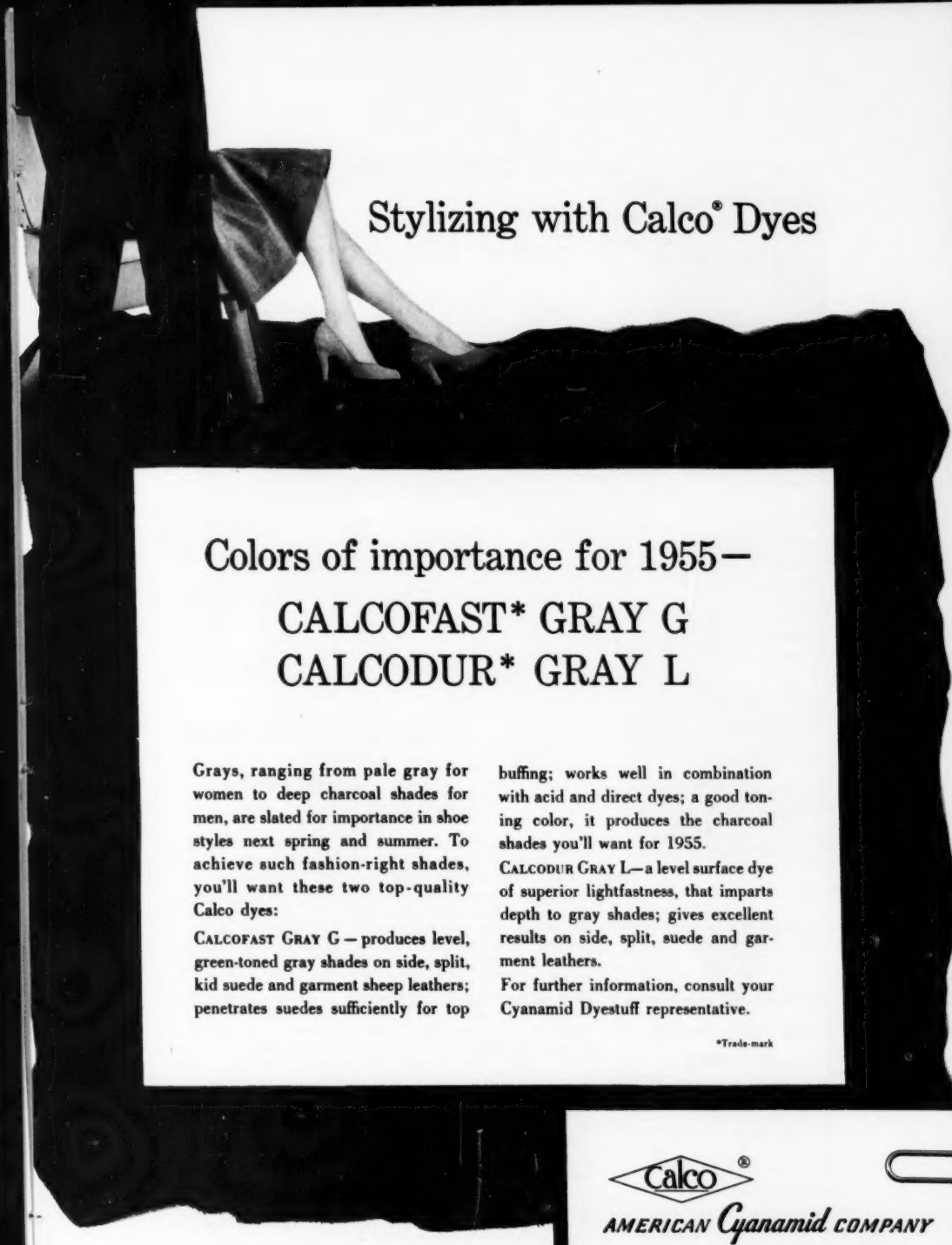

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CALCODUR* GRAY L

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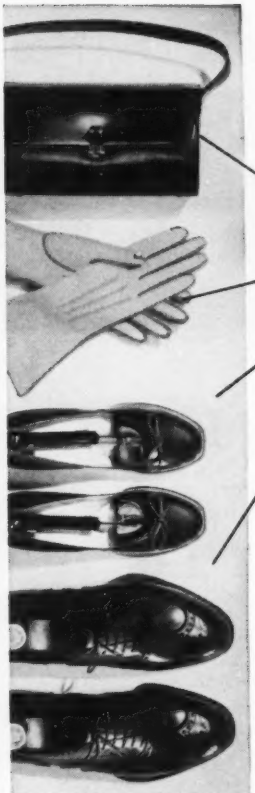

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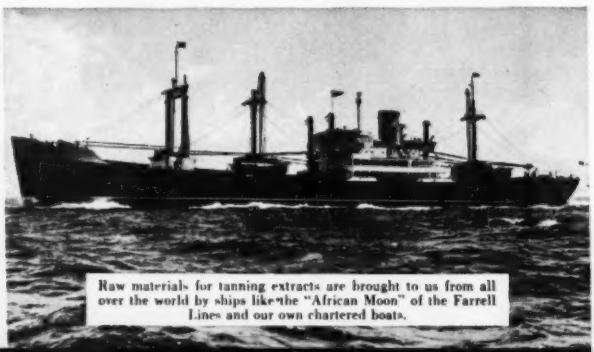

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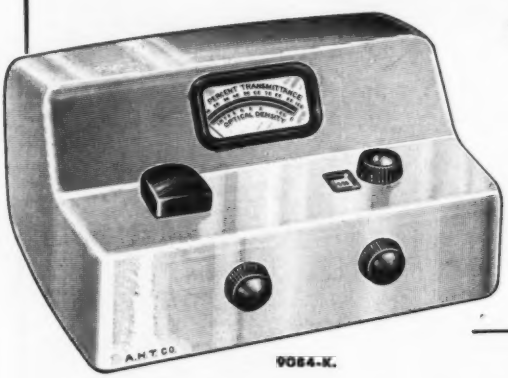

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VOL. XLIX DECEMBER 1954 No. 12

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CONVENTION NOTICE

The 1955 annual meeting will be held at the New Ocean House, Swampscott, Massachusetts on May 22-23-24-25.

All persons who desire to present papers are advised to submit a brief abstract of the paper to:—

Mr. D. Meo, Chairman
Convention Committee
c/o Salem Oil and Grease Company
Salem, Massachusetts

All abstracts must be in by February 28, 1955.

Photograph by BACHRACH

L. H. LINCOLN

L. H. Lincoln, founder and president of L. H. Lincoln and Son, died at his home in Coudersport, Penna. on October 10 at the age of 71. He had been a member of our Association since 1926.

Lee, as he was known to his host of friends, entered the tanning industry as a young man, and served his apprenticeship with Endicott-Johnson. His

introduction to the art of tanning was contemporaneous with the establishment of the Endicott Tannery. Later Lee operated tanneries in the United States and Canada. The marketing of extracts and auxiliary tanning materials appealed more to him than the manufacture of leather so, following his natural bent, he entered the marketing field on his return from Canada. For a number of years he represented various extract importers and manufacturers supplying the leather industry. His knowledge of tanning, along with his genial personality, contributed materially to his success in these endeavors. Because of his knowledge of extracts, he served his Government as advisor in these materials during World War I. In 1935, Lee established his own business in Coudersport, Penna. which was located in the center of the sole leather industry.

During his life in Coudersport, he took an active interest in all worthy community affairs. Among a few of these were the founding of the Coudersport Golf Club, the improvement in the physical plant and personnel of the Community Hospital, the procurement of new industries for the town, and the placement of the railroad serving the community on a healthier financial and operating basis. His enthusiasm for Rotary International was well known. During his term as District Governor, he instituted the Citizens of Tomorrow program by which tangible interest is shown in promising young men of high school age. The program, throughout the District, has been intrumental in inducing a number of boys to continue their education through college.

For the past few years failing health had curtailed his activities but, prior to this, he was a regular attendant at our Annual Meetings. He took a real interest in Association affairs and was generous in his support of the organization.

Lee loved everything wholesome—the outdoors, fishing, hunting, golf, horses, dogs—but his greatest love was for his home, his family, and his friends. This attribute of affection was expressed in his genial laugh and his kindly bearing. His death marks the passing of a man of integrity, uprightness of character, and fairness in dealing with his fellow man.

He was laid to rest in the Saint Eulalia burial grounds in Coudersport. He is survived by his widow, a son Howard, a daughter, a grandson and granddaughter, a great granddaughter, and by his mother. To them his numerous friends extend the deepest sympathy in their bereavement.

Dean Williams

BUREAU OF EMPLOYMENT

Wanted chemist, experienced in Leather Technology for research and development in chrome and vegetable sole and insole leathers. Write full details to Brockton Cut Sole Corporation, 53 Spark Street, Brockton 68, Massachusetts.

Position Wanted: Chemist and sulphonator with over twenty-five years experience in manufacturing, analysis, and control testing of sulphated and leather oils. Address replies to Box CH177, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

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Estimation of Sulfur in Proteins in General and Leather in Particular.

By P. HANUMANTA RAO

Swedish Tanning Research Institute
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Most methods of sulfur estimation are carried out by oxidizing the sulfur to sulfate and then precipitating and weighing it as barium sulfate. Various reagents have been used to oxidize sulfur in leather (proteins), like nitric acid [1] and perchloric acid. However, Mörner [2] found that the oxidation of proteins in such media yielded methyl sulfonic acid which would form soluble barium salts and thus gave low values. He actually obtained the following values for sulfur in collagen by different oxidizing agents: alkaline oxidation 0.3 to 0.5 per cent, oxidation with conc. nitric acid 0.02 per cent, with fuming nitric acid 0.01 per cent, with aqua regia 0.02 per cent. The low values for sulfur may be due to the oxidation in acid medium. Grote-Krekeler [3] method

gives generally good values, but may sometimes give lower values due to the presence of much inorganic matter which retains some sulfate in the ash. The bomb method is the best [4], but small laboratories do not have the bomb.

So, a simple method, suggested by Dr. Gustavson, was tried and found suitable for sulfur estimation in leather, specially vegetable retanned chrome and syntan tanned.

Method

A suitable quantity (0.4 to 0.8 g) of leather or other protein, depending on the sulfur content, is mixed with a small quantity of distilled water so that it is just moist and not too wet, in a nickel crucible. This is heated on a Bunsen burner slowly and sodium peroxide (analytical quality) is added little by little and the heating continued carefully. The lid of the crucible is kept ready to close when the material catches fire and starts burning with a sparkling noise. Care is taken that the burning is not too violent by adjusting the rate at which the sodium peroxide is added and regulating the flame heating the crucible. After the sample has completely burned, a little excess of sodium peroxide is added and the heating continued, with the lid closed, for a few minutes. The crucible is then grasped with the tongs and a slow rotatory motion is given so that the molten contents will spread over the sides and help to bring down and oxidize any particles that escaped oxidation. It is heated for a few minutes more than then the contents are allowed to cool a little.

The crucible and the lid are placed in a clean dry beaker and boiling water is poured carefully from the side, keeping the beaker covered with a watch glass. The crucible and the lid are washed with 1:1 hydrochloric acid into the beaker. The contents of the beaker are acidified with conc. hydrochloric acid and the solution filtered into another beaker. This filtered solution is brought to boil and the sulfate determined as usual by precipitation and weighing as barium sulfate.

A few samples of hide powder tanned in different ways have been analysed by the Grote-Krekeler and the sodium peroxide oxidation methods. The results are tabulated below.

Hide powder tanned with	SULPHUR %	
	Grote-Krekeler	Sodium peroxide
Syntan , (Hg 6)	1.55	1.52
Syntan II (Novolac)	2.30	2.30
Syntan III (Tanigan F C)	2.80	2.90
Chrome sulfate liquor	1.60	1.60
Vegetable retanned (chrome)	0.44	0.43

The method has been used in this laboratory for various types of hide powder and leather and found suitable as a quick, reliable and accurate method, after obtaining the necessary skill in the manipulation of the method, which may be obtained with a little experience.

The author wishes to express his thanks and indebtedness to Dr. K. H. Gustavson, Director, Swedish Tanning Research Institute, under whose inspiring guidance the work was done. He also acknowledges with gratitude the grants made by the Government of India and the Statens Tekniska Forskningsrad, which made this work possible.

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A Method of Producing Unhairing Liquors from Staple-Rayon Wastes.

By INGULF SKOGESTAD

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The viscose process is a heavy consumer of chemicals. To produce a ton of rayon, one needs about three times the quantity of sulfuric acid, sodium hydroxide and carbon disulfide. There are, however, waste products from the process which can be utilized, the most important one being hydrogen sulfide. These wastes are by simple absorption easily converted to an efficient unhairing solution suitable for use in tanneries.

The conventional procedure for the preparation of viscose further results in large amounts of caustic soda wastes, which mostly have to be discarded. The caustic originates from the steeping operation. During the steeping operation, where bleached sulfite-cellulose is steeped in sodium hydroxide solution of mercerising strength, hemicellulose is removed from the cellulose.

It is vital for the viscose process that the hemicellulose content of the steeping solution should be kept low. As it is not economical to discard the used caustic, common practice is to remove the hemicellulose from a portion of the solution by dialysis, and return the caustic to the process. In this way a fairly low concentration of hemicellulose is maintained in the steeping solution. There is, however, a limit for the reuse of the caustic, resulting in an available supply of cheap caustic solutions.

In the spinning bath, the xanthate is forced to decompose directly by the effect of mineral acids and neutral salts, cellulose being thereby both coagulated and regenerated. At the same time, the free alkali is neutralized and the byproduct salts are decomposed with the liberation of H_2S, CS_2, CO_2 and free sulfur. As the temperature of the bath is maintained between 45° - 55° C., the amount of CS_2 liberated is mainly in a gaseous state. Of these gases, H_2S is liberated in by far the greatest quantity.

If these sulfur-containing vapors are absorbed in sodium hydroxide, the resulting solution will have unhairing properties. This absorption is easily brought about by washing the vapors in the conventional manner with the caustic solution used in the steeping operation. The resulting unhairing liquor will consequently contain a certain amount of hemicellulose. The hemicellulose, however, has no influence on the unhairing properties of the liquor.

During this absorption, the following components will be formed: sodium hydrogen sulfide, sodium sulfide, soda, thiosulfate and hemicellulose. Sodium sulfide results from the absorption of hydrogen sulfide since $H_2S + 2NaOH = Na_2S + 2\,H_2O$; which, by further reaction gives hydrosulfide: $H_2S + Na_2S = 2\,NaHS$. Carbon dioxide reacts to form sodium carbonate: $CO_2 + 2\,NaOH = Na_2CO_3 + H_2O$. There is a possibility for the formation of a small amount of thiocarbonate: $3\,CS_2 + 6\,NaOH = 2\,Na_2CS_3 + Na_2CO_3 + 3\,H_2O$. Sodium thiocarbonate reacts with an excess of sodium hydroxide forming hydrosulfide: $Na_2CS_3 + 3\,NaOH = 3\,NaHS + Na_2CO_3$. Thiocarbonate will, of course, react similarily with lime with the formation of $Ca(HS)_2$ and should, therefore, behave as a mild depilator. Thiosulfate will be formed in smaller amounts due to an inevitable oxidation which, simplified, may be visualized by the reaction: $2\,NaHS + 2\,O_2 = Na_2S_2O_3 + H_2O$. If the washing liquor is added in an amount just enough to be neutralized, the resulting liquor will thus contain Na_2S, NaHS, Na_2CO_3 and Na_2CS_3 with hemicellulose from the original solution.

For the past few years a paper plant in Scandinavia has been producing a similar unhairing liquor, which is being used by the tanners in increasing amounts. In action, this liquor has properties intermediate between those of NaHS and Na_2S, and has given very satisfactory results. Besides, this unhairing liquor is very cheap. The production follows the principles just out-

lined, and the waste vapors are absorbed in the conventional manner in efficient washing towers. The possibilities of varying the composition of the product are great, so that depilators of varying strengths and plumping effect can easily be made. The great advantages are easily seen, and an ideal unhairing liquor combining the best properties of NaHS and of Na_2S can be made without difficulty.

As an example, table 1 gives some typical analytical values of unhairing liquor produced by this process. To make it easier for comparison, the sulfur

TABLE I

Unhairing Liquor No.		1	2	3	4
Na_2S	g/l	39.0	59.8	39.4	67.2
NaHS	g/l	194.9	166.3	176.6	153.2
Total NaHS	g/l	222.9	209.2	204.9	201.5
Na_2CO_3	g/l	20.1	20.4	21.4	19.6
Total NaOH orig.	g/l	190.4	198.0	189.0	195.2
NaOH bound to S & CO_2 (calc.)	g/l	194.0	195.5	182.0	192.7
Specific Gravity		1.177	—	1.170	—
pH		10.9	—		—

content of Na_2S is calculated as NaHS and added to the real NaHS content, the result giving the total NaHS. These four liquors are taken from a series of trials which showed that all liquors with a total NaHS content above 200 g/l, gave similar and comparable unhairing results when used in the same amounts. Theoretically, about 2 liters of these liquors equalizes 1 kg. Na_2S (60 per cent). In practice, however, it was found necessary to use a slight excess of liquor, e.g. 2.5 liter gave the same unhairing results in the same time as 1 kg. sodium sulfide. This means that a liquor with an analytical composition falling between the limits shown in table 1 can be used in the tanneries as a depilator with constant properties. It is, therefore, fairly simple to keep the liquor constant during the production. Generally, the following composition represents an unhairing solution with constant properties:

ca. 150 – 180 g/l NaHS
ca. 40 – 70 g/l Na_2S
ca. – 20 g/l Na_2CO_3
ca. 2 – 3 g/l $Na_2S_2O_3$
ca. – 30 g/l hemicellulose

This solution is a clear, brownish colored liquor with a characteristic odor. Both the soda and the thiosulfate react with lime giving sodium hydroxide, thereby increasing the causticity. A variation in Na_2S content from 40 - 70 g./l. will not effect the plumping properties of the liquor. With a drum process, normally about 5 - 6 per cent of unhairing liquor will be used. A sulfide

content of 4 per cent in this liquor means a real sulfide concentration in the drum of 0.2 per cent increasing to 0.35 per cent when the Na_2S content reaches the upper limit.

The soda content of the liquor keeps almost constant, varying about 2 per cent. The thiosulfate content is negligible, being about 2-3 g./l. "Total NaOH orig." is the concentration of the washing liquor, being about 19 per cent. This steeping liquor contains very close to 30 g./l. of hemicellulose.

There is always a tendency for the hemicellulose to be "salted out" on standing, this tendency being greater the larger the hydrosulfide content and the lesser the Na_2S content. In very cold weather, of course, the Na_2S may solidify to some extent. The hemicellulose which is salted out is dark in color and sludgy. Under normal conditions, these inconsistencies cause no inconvenience.

Received May 4, 1954.

Tannin Evaluation of One Hundred Sixty-Three Species of Plants

By M. L. Happich, C. W. Beebe and J. S. Rogers

*Eastern Regional Research Laboratory**
Philadelphia 18, *Pennsylvania*

For a number of years the United States Department of Agriculture has been interested in the development of new domestic sources of vegetable tanning materials and has previously reported on the possible utilization of hemlock bark [1], Sitka spruce bark [2], Florida scrub oak barks [3], Tennessee Valley Oak barks [4], sumac leaves [5], and canaigre tubers [6].

We have recently had an opportunity for the tannin evaluation of a large number of plant species received at this laboratory for examination for steroidal sapogenins. In addition to this determination, qualitative tests have been made for flavanols, alkaloids, sterols, phenols, and tannin. Some

*A Laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

of these results have been reported in two publications [7, 8]. The Hides, Tanning Materials and Leather Section has made analyses of those plants which gave favorable qualitative tests for tannin and of which there was sufficient available material. The analyses were made by the official methods of the American Leather Chemists Association [9], modified by varying the hide powder used in proportion to the tannin content.

In the cortisone survey it was not necessary or possible to obtain representative specimens of every plant family, nor to obtain samples of every portion of a specimen. Therefore, the results of the tannin survey are necessarily incomplete. Analyses, showing tannin content and purity, afford a preliminary screening process for new materials. However, other requirements must be met before the suitability of a material for the production of a commercial tanning extract can be established.

1. The material must be cheaply available, either actually or potentially, in sufficient quantities for the operation of an extract plant.
2. Facilities for power, water, labor and transportation for an extract plant must be easily available.
3. It must be possible to extract the tannin cheaply to give an extract producing satisfactory leather.

It is doubtful if a tanning extract could be produced economically from material containing less than 10 per cent tannin, if the material was used solely as a source of tannin. If it has other uses, so that the tannin could be regarded as a by-product or a co-product, the minimum tannin requirement might be reduced to 8 per cent. In any case, the purity should be above 50.

From the first 2,000 plant collections examined, about 1,823 were eliminated by the preliminary qualitative tests as containing little or no tannin. Of the remaining 177, 69 were analyzed. Of these 16, or 23 per cent, contained more than 8 per cent tannin and had purities above 50. Of these 16, two species of Terminalia, the Caesalpinia and the Eucalyptus either are now used for tanning or are closely related to species now being used.

Table 1 gives the data on the 16 samples analyzed which appeared most promising. Table II gives the data on the remainder of the analyzed samples. Table III gives data on samples which appeared promising by the preliminary screening tests but which could not be analyzed because of an insufficient amount of sample. The botanical identification of those plants taken from the first 1,000 collections is from the publications previously mentioned [7, 8]. Data on the remaining 1,000 collections have not yet been published, but identifications are by the same authors. Some data on common names, habitat, etc. are taken from Bailey [10]. Data on the original sources of the plants

and of the sources of the specimen samples are given to indicate the optimum location for cultivation, if desired.

There are 108 samples listed in Table III. Using the figure of 23 per cent obtained from Table I and II it might be assumed that about 25 of these samples would pass the analytical screening test. This would give a total of 41 from the original 2,000 specimens.

Further work on one of the samples indicates that, in addition to tannin analysis, a more detailed study is necessary in order to determine the potential value of a plant product as a source of tannin. The rhizomes of smilax, *Smilax laurifolia*, contained 15.4 per cent tannin and had a purity of 57.94. The plant is abundant and easily grown along the Atlantic coast of the United States. Since these conditions are favorable, further tests were made of this material. It was found, however, that the rhizomes would be difficult and expensive to harvest because of their configuration. Comminution would be expensive, inasmuch as wet shredding is difficult, and the dry material is extremely hard. Furthermore, tannin extraction was slow and inefficient and the extract produced was poor, having a tendency to gelatinize. Penetration during tannage was slow and the leather produced was of poor color with a harsh, rough grain. It is doubtful even though the material has a favorable tannin analysis, that a satisfactory extract could be produced.

The results of these tests cannot be taken as a complete tannin survey. However, some conclusions may be drawn as to the presence of tannin-bearing species in the various families. Of more than 500 species of Amaryllidaceae, none contained more than insignificant amounts of tannin. Of more than 300 species of Liliaceae only a few species of Smilax, Urginea and Nolina contained tannin. Very few species of Bignoniaceae, Compositae, Dioscoreaceae, Oleaceae, Palmaceae, or Solanaceae contained appreciable amounts of tannin. High proportions of tannin-bearing species were found in the Aceraceae, Anacardiaceae, Betulaceae, Caprifoliaceae, Hamamelidaceae, Iridaceae, Leguminosae, Myrtaceae, Rosaceae, Sapindaceae, Sapotaceae, and Saxifragaceae. It was not possible to draw conclusions about other families.

Acknowledgment

The authors acknowledge with thanks the assistance of F. P. Luvisi in conducting the analytical work in this evaluation. They also wish to thank the Biochemical Section of the Eastern Utilization Research Branch and the Section of Plant Introduction of the Horticultural Research Branch, Agricultural Research Service, for providing the plant samples used in this research from their cooperative cortisone program.

TABLE I

Data On Samples Shown As Promising By Analysis.

Botanical Name and Common Name if Known	Habitat	Part of Plant Analyzed*	Source of Material Analyzed	(Results Calculated to Moisture-Free Basis) Tanin Analysis Total Extractive %	Soluble Extractive %	Insolubles in Extractive %	Non-tannin %	Tannin %	Purity Basis Sol. Ext.
Combretaceae									
Terminalia chebula, Myrobalams	Asia	le, in	Coconut Grove, Fla.	46.47	42.49	3.98	18.48	24.01	56.51
Terminalia muelleri	Asia	le, st, fr.	Coconut Grove, Fla.	38.74	34.03	4.71	13.10	20.93	61.50
Iridaceae									
Watsonia fulgens, Watsonia	South Africa	bu	Viljoeas Pass, C.P.	45.86	41.58	4.28	16.08	25.50	61.33
Leguminosae									
Caesalpinia ferrea	Caesalpinia native to warm regions of both hemispheres	le, in	Coconut Grove, Fla.	37.85	35.21	2.64	17.41	17.80	50.55
Calliandra haematocephala	Tropics	le, fr.	Coconut Grove, Fla.	26.22	24.08	2.14	11.78	12.30	51.80
Cassia nictitans	Warm parts of world	w.p. (2)	Raleigh, N. C.	32.71	30.36	2.35	11.43	18.94	62.37
Peltophorum inereme	Australia, Philippines	le, fr.	Coconut Grove, Fla.	31.20	26.67	4.53	11.29	15.38	57.67
Liliaceae									
Smilax laurifolia, Smilax	N. J. south to Fla. & Texas	rh.	Southport, N. C.	28.55	26.58	1.97	11.18	15.40	57.94
Malpighiaceae									
Byrsonima crassifolia	Trop. America, Mex. & So.	le, st, fr.	Coconut Grove, Fla.	26.96	23.25	3.71	10.87	12.39	53.29
Meliaceae									
Swietenia mahagoni, Mahogany	Tropical regions of N. & S. America, W. Indies & S. Fla.	le, fr.	Coconut Grove, Fla.	27.12	23.89	3.23	11.04	12.85	53.79
Myrtaceae									
Eucalyptus obtusifolia	Most Eucalyptus are native to Australia	le	Coconut Grove, Fla.	30.46	29.15	1.31	13.74	15.41	52.86
Eucalyptus paulistana		le, fr.	Coconut Grove, Fla.	31.56	30.19	1.37	14.68	15.51	51.37
Eucalyptus staigeriana		le, fr.	Coconut Grove, Fla.	39.18	37.05	2.13	14.55	22.50	60.73
Syzygium cumini	Tropics of Old World	le, fr.	Coconut Grove, Fla.	33.14	25.93	7.21	12.60	13.30	51.29
Palmae									
Serenoa repens, Saw Palmetto	Coastal Plain, S. E. United States	in.	7 mi. S.W. of Jessup, Georgia	20.80	19.90	0.90	9.32	10.58	53.17
Sapindaceae									
Koelreuteria formosana	Formosa	le, fr.	Coconut Grove, Fla.	28.28	27.56	0.72	13.63	13.93	50.54

*bu - bulk; fl. - flower; fr - fruit; ib - inflorescent bud; in - inflorescence; le - leaves; rh - rhizomes; st - stems; ro - roots; tu - tubers; tw - twigs; wp - whole plant; (1) young plant, (2) plant in fruit, (3) plant flowering and fruiting.

TABLE II

Analyses of Plant Specimens—In Addition to Those Shown in Table I.

Botanical Name and Common Name if Known	Habitat	Part of Plant Analyzed*	Source of Material Analyzed	(Results Calculated to Moisture-Free Basis) Total Extractive %	Tannin Analysis Soluble Extractive %	Insolubles in Extractive %	Non-tannin %	Tannin %	Purity Basis Sol. Ext.
Aceraceae									
Acer truncatum, Maple species	N. China	le	Chico, California	26.99	25.24	1.75	16.09	9.15	36.25
Anacardiaceae									
Pistacia chinensis, Chinese Pistachio	China	le	Chico, California	37.41	35.38	2.03	23.14	12.24	34.60
Pistacia lentiscus, Mastic tree of Chios	Mediterranean region	le	Chico, California	46.89	42.87	4.02	27.76	15.11	35.25
Pistacia vera, Pistachio	Mediter. reg. & Orient	le	Chico, California	34.27	32.90	0.37	24.08	8.81	26.78
Apocynaceae									
Apocynum cannabinum, Indian hemp	Northern states of United States	fr.	Raleigh, N. C.	25.92	23.94	1.98	13.96	9.98	41.69
Carissa grandiflora, Natal plum	South Africa	le	U. S. Hort. Field Sta. La Jolla, Calif.	38.18	36.78	1.40	22.29	14.49	39.37
Cistaceae									
Cistus crispus, Rock Rose	S. W. Europe	le	Chico, California	31.12	29.47	1.65	19.70	9.77	33.15
Cistus monspeliensis, Rock Rose	Mediterranean region	le	Chico, California	31.57	30.38	1.19	17.35	13.03	42.89
Cochlospermaceae									
Amoreuxia sp.	Tropical regions	ro	Navajoa, Son., Mex.	22.77	20.18	2.59	12.88	7.30	36.17
Combretaceae									
Terminalia arjuna	Central and South Asia	le, fr.	Coconut Grove, Fla.	26.93	24.85	2.08	16.00	8.85	35.61
Dioscoreaceae									
Dioscorea composita	Dioscoreo species in warmer regions of eastern and	rh.	Oaxaca, Mexico	64.52	59.56	4.96	55.71	3.85	6.46
Dioscorea sp.	western hemispheres	tu	Barrancas, Jal., Mex.	—	25.28	—	15.40	9.88	39.08
Ebenaceae									
Diospyros sp., Persimmon	Many species in Asia	fr., le	Coconut Grove, Fla.	28.22	25.13	3.09	16.65	8.48	33.74
Ericaceae									
Arbutus andrachne, Arbutus	Greece and Orient	le	Chico, California	42.93	40.17	2.76	26.79	13.38	33.31

*bu - bulk; fl. - flower; fr - fruit; ib - inflorescent bud; in - inflorescence; le - leaves; rh - rhizomes; st - stems; ro - roots; tu - tubers; tw - twigs; wp - whole plant; (1) young plant, (2) plant in fruit, (3) plant flowering and fruiting.

TABLE II (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Analyzed*	Source of Material Analyzed	(Results Calculated to Moisture-Free Basis) Tannin Analysis Total Extractive %	Soluble Extractive %	Insolubles in Extractive %	Non-tannin %	Tannin %	Purity Basis Sol. Ext.
Ericaceae (continued)									
Kalmia latifolia, Mountain or Am. laurel, Calico bush	North America	le, fr.	Highlands, N. C.	36.67	32.26	4.41	16.86	15.40	47.74
Oxydendrum arborem, Sour-wood or Sorrel tree	East. No. America	One sample le and one fr. identification lost.	Raleigh, N. C.	33.22	31.71	1.51	21.87	9.84	31.03
Oxydendrum arboreum, Sour-wood or Sorrel tree				11.87	11.20	0.67	8.35	2.85	25.45
Rhododendron maximum, Great laurel	North America	le, fr.	Highlands, N. C.	30.17	27.39	2.78	15.00	12.39	45.24
Euphorbiaceae									
Aleurites fordii, China wood-oil tree	Asia	le	Chico, California	33.83	32.83	1.00	21.34	11.50	35.03
Fagaceae									
Castanea mollissima, Chinese chestnut	North & West China	le	Chico, California	36.07	34.31	1.76	22.26	12.05	35.12
Judlandaceae									
Carya illinoensis, Pecan	Central U. S. & Mexico	wp (1)	Chico, California	50.74	49.20	1.54	37.70	11.50	23.37
Leguminosae									
Caesalpinia pulcherrima, Barbados Pride, Barbados flower, Fence Dwarf Poinciana	Generally in tropics	le, fr, in.	Coconut Grove, Fla.	32.48	30.98	1.50	19.65	11.33	36.57
Cassia fistula, Pudding Pipe tree, Golden Shower	India	le, fr.	Glen Dale, Maryland	29.81	27.96	1.85	23.77	4.19	14.98
Cassia marginata	Many Cassia in warmer parts of the world	le, fr	Coconut Grove, Fla.	36.92	35.62	1.40	23.77	11.85	33.27
Cassia renigera	Many Cassia in warmer parts of the world	le, in.	Coconut Grove, Fla.	32.11	30.72	1.39	15.85	14.87	48.40
Ceratonia siliqua, Carob	Widely distributed in warm countries	fr.	Coconut Grove, Fla.	40.90	39.06	1.84	30.82	8.24	21.10

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TABLE II (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Analyzed*	Source of Material Analyzed	(Results Calculated to Moisture-Free Basis) Total Extractive %	Tannin Analysis Soluble Extractive %	Insolubles in Extractives %	Non-tannin %	Tannin %	Purity Basis Sol. Ext.
Leguminosae (Continued)									
Cercis canadensis, red bud, Judas tree	United States	le.	Raleigh, N. C.	43.30	39.74	3.56	26.36	13.38	33.67
Haematoxylon campechianum, Compeachy wood, logwood	Mexico, Central America, West Indies	le, in.	Coconut Grove, Fla.	20.93	19.79	1.14	13.10	6.69	33.80
Piptadenia macrocarpa, Acacia grata	Brazil, Bolivia	le, fr.	Coconut Grove, Fla.	29.99	26.72	3.27	16.87	9.85	36.86
Schotia transvaalensis	Subtropic and S. Africa	le	Coconut Grove, Fla.	25.76	23.16	2.60	14.24	8.93	38.56
Liliaceae									
Nolina cf. juncea	Nolina species are desert plants	wp	Dur. Mex.	47.78	47.26	0.52	41.16	6.10	12.91
Myricaceae									
Myrica carolinensis, Bayberry	Nova Scotia to Fla. and Ga., Shores of Lake Erie	le, fr.	Raleigh, N. C.	14.95	13.76	1.19	6.83	6.93	50.36
Myrtaceae									
Eucalyptus alba, Poplar gum	Probably Australia	le, fr.	Coconut Grove, Fla.	24.87	23.07	1.80	12.50	10.57	45.82
Feijoa sellowiana, Pineapple guava	South America	le	Chico, California	24.48	22.30	2.18	14.09	8.21	36.82
Feijoa sellowianna, T.B. Pineapple guava	South America	le	Chico, California	29.45	28.07	1.38	16.97	11.10	39.54
Psidium guajava, Guava of the tropics	Native to tropical and subtropical America. Naturalized in parts of Asia an Africa	le, fr.	Coconut Grove, Fla.	26.98	23.52	3.46	14.43	9.09	38.65
Psidium littorale		le, fr.	Coconut Grove, Fla.	24.75	22.54	2.21	11.57	10.97	48.67
Onagraceae									
Oenothera biennis, European evening primrose	Introduced into Europe from Amer. Weed in Old World	wp., fr.	Beltsville, Maryland	28.44	26.34	2.10	15.26	11.08	42.07

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TABLE II (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Analyzed*	Source of Material Analyzed	(Results Calculated to Moisture-Free Basis) Total Extractive %	Tanin Analysis Soluble Extractive %	Insolubles in Extractives %	Non-tannin %	Tannin %	Purity Basis Sol. Ext.
Orobanchaceae									
Epifagus virginiana		wp (3)	Beltsville, Maryland	47.47	39.66	7.81	24.01	15.65	39.46
Pittosporaceae									
Pittosporum pentandrum		le	Coconut Grove, Fla.	28.64	27.88	0.76	17.03	10.85	38.92
Rosaceae									
Adenostoma fasciculatum, Heathlike evergreen shrub	California	le	Murrieta, Calif.	39.09	37.17	1.92	23.03	14.15	38.07
Crataegus douglasii, Crataegus, hawthorn	Br. Col. and N. Calif. to Wyoming	le, fr.	Chico, California	40.56	38.87	1.69	35.43	3.44	8.85
Crataegus durobrivensis, Crataegus hawthorn		le	Chico, California	30.23	28.47	1.76	22.60	5.88	20.65
Crataegus lavallei	Possibly same as Carrierei which orig. in France	le	Chico, California	35.35	31.91	3.44	25.67	6.24	19.56
Eriobotrya japonica, Loquat	China and Japan. Much planted in Gulf States	le, fr.	Coconut Grove, Fla.	29.06	28.59	0.47	22.43	6.16	21.55
Malus kaido, apple sp.	Northern hemisphere	le	Chico, California	44.06	39.36	4.70	28.90	10.46	26.58
Malus kaido, apple sp.	Northern hemisphere	le	Chico, California	44.56	42.99	1.57	31.05	11.94	27.77
Rubiaceae									
Ixora coccinea	East Indies	le, st, in.	Coconut Grove, Fla.	24.86	22.79	2.07	16.54	6.25	27.42
Sapindaceae									
Dimocarpus longan		fr.	Coconut Grove, Fla.	30.21	28.63	1.58	19.50	9.14	31.92
Sapotaceae									
Achras sapota, Sapodilla	American tropics	le, fr.	Coconut Grove, Fla.	35.75	32.51	3.24	24.88	7.63	23.47
Lucuma salicifolia	American tropics	le, fr.	Coconut Grove, Fla.	37.13	33.08	4.05	25.34	7.74	23.40
Mimusops balata	West Indies	le	Coconut Grove, Fla.	28.86	26.97	1.87	16.00	10.97	40.67
Scrophulariaceae									
Chelone lyonii	E. and Central U. S.	st, le, fr	Highlands, N. C.	21.17	19.80	1.37	10.00	9.80	49.49

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TABLE III

Data On Unanalyzed Samples Passing Preliminary Screening Tests

Botanical Name and Common Name if Known	Habitat	Part of Plant Tested*	Source of Material Tested
Aceraceae			
Acer carpinifolium, Hornbeam maple	Temperate zones	le	Coconut Grove, Florida
Acer miyabei	Japan	le	Glenn Dale, Maryland
Anacardiaceae			
Pistacia lentiscus, Mastic tree	Mediterranean region	fr	Chico, California
Schinus terebinthifolius, Pepper tree	Brazil	le, st	Coconut Grove, Florida
Aquifoliaceae			
Ilex sp., Holly	Temperate & Tropic zones	le	Glenn Dale, Maryland
Betulaceae			
Alnus japonica, Alder	Japan	le	Glenn Dale, Maryland
Carpinus cordata	Japan, Korea	le	Glenn Dale, Maryland
Carpinus tschonoskii	China (?)	le	Glenn Dale, Maryland
Calycanthaceae			
Calycanthus floridus, Carolina Allspice	North America	le	Glenn Dale, Maryland
Caprifoliaceae			
Abelia grandiflora, Abelia	General cultivation	le, fl	Glenn Dale, Maryland
Diervilla "richesse", Weigela	E. North America	le, fl	Glenn Dale, Maryland
Viburnum kansuense	W. China	le, fl	Glenn Dale, Maryland
Viburnum macrocephalum, Chinese snowball	China	fr	Glenn Dale, Maryland
Celastraceae			
Euonymus phellomana, Spindle tree	Central & East Asia	le	Glenn Dale, Maryland
Tripterygium wilfordii	Manchuria, Japan	le, fr	Glenn Dale, Maryland
Cunoniaceae			
Weinmannia sp.	South America	wp	Colombia, So. America
Cyrillaceae			
Cyrilla racemiflora, Leatherwood	North Carolina to Fla. to Texas	le	Glenn Dale, Maryland
Dilleniaceae			
Actinidia chinensis	East Asia	le	Glenn Dale, Maryland
Dioscoreaceae			
Dioscorea composita,	Central America	tu	Mexico City
Dioscorea polygonoides	Central America	tu	Puerto Rico
Dioscorea sativa	Central America	le	El Salvador
Dioscorea sp.	Central America	rh, le, tu	South Africa
Ebenaceae			
Diospyros kaki, Persimmon	Mexico, West Indies	le	Chico, California
Elaeagnaceae			
Hippophae rhamnoides Sea buckthorn	Europe, W. & C. Asia	le	Glenn Dale, Maryland

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TABLE III (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Tested*	Source of Material Tested
Ericaceae			
Enkianthus campanulatus	Japan	le	Glenn Dale, Maryland
Kalmia latifolia American laurel	North America	le, fr	Glenn Dale, Maryland
Leucothoe sp.	N. & S. America, Asia	le	Glenn Dale, Marylond
Eucommiaceae			
Eucommia ulmoides	Central China	le	Glenn Dale, Maryland
Fagaceae			
Quercus acutissima Oak	Japan, Korea	le, tw, fr	Glenn Dale, Maryland
Hamamelidaceae			
Fortunearia sinensis	China	le	Glenn Dale, Maryland
Hamamelis vernalis Witch hazel	Mo. to La. to Okla.	le, fr	Glenn Dale, Maryland
Loropetalum chinense	C. & S. E. China	le	Glenn Dale, Maryland
Parrotia persica	Persia	le	Glenn Dale, Maryland
Hypericaceae			
Hypericum patulum	Japan	le, fl, fr	Beltsville, Maryland
Iridaceae			
Watsonia wilmsii, Watsonia	South Africa	bu	South Africa
Lauraceae			
Sassafras albidum Sassafras	Massachusetts to N. C. to Ky.	le	Glenn Dale, Maryland
Leguminosae			
Acacia baileyana, Acacia		le	Chico, California
Acacia melanoxylan Blackwood acacia	Cult. in California	le	Chico, California
Acacia pycnantha		le	Chico, California
Albizzia lebbekoides Lebbec tree	Tropics	le, st	Coconut Grove, Florida
Caesalpinia ferrea	Tropics	le, fl	Coconut Grove, Florida
Caesalpinia pulcherrima	Tropics	le, fl, fr	Coconut Grove, Florida
Cassia marginata	Warmer parts of world	le, st	Coconut Grove, Florida
Cassia nictitans	Warmer parts of world	wp, fr	Raleigh, North Carolina
Cassia renigera	Warmer parts of world	le, fl	Coconut Grove, Florida
Ceratonia siliqua, Carob St. John's Bread	Mediterranean	fr, fl	Coconut Grove, Florida
Ceris canadensis		le	Raleigh, North Carolina
Cercis siliquastrum, Red Bud Judas tree	S. E. Europe	le	Chico, California
Gymnocladus chinensis	China	le	Glenn Dale, Maryland
Haematoxylon campechianum Haematoxylon		le, fl	Coconut Grove, Florida
Indigofera chinensis incarnata Indigo	China	le	Glenn Dale, Maryland
Peltogyne nitens		le, fr	Coconut Grove, Florida

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TABLE III (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Tested*	Source of Material Tested
Leguminosae (Continued)			
Wisteria floribunda Wisteria	Japan	fr	Glenn Dale, Marylond
Liliaceae			
Albuca sp.	South Africa	le	Cape Province, Africa
Nolina georgiana	Tropics	le, st	Raleigh, North Carolina
Nolina microcarpa		wp	Oracle, Arizona
Scilla sp., Squill	World-wide	bu	Transvaal
Smilax auriculata, Smilax	Eastern United States	rh	Southport, No. Carolina
Smilax mexicana	Mexico	rh	Jalcocotan, Mexico
Urginea burkei, Urginea		bu	Transvaal
Lythraceae			
Lagerstroemia indica Crape Myrtle	China	le, fl	Glenn Dale, Maryland
Lawsonia inermis, Henna	North Africa	le, st, fr	Savannah, Georgia
Magnoliaceae			
Liriodendron tulipifera Tulip tree	North America	le, st	Silver Spring, Maryland
Magnolia stellata Magnolia	Japan	le	Glenn Dale, Maryland
Moraceae			
Coussapoa sp. Coussapoa	Trop. S. America	le	Colombia
Myricaceae			
Myrica rubra Wax myrtle	China, Japan	le	Savannah, Georgia
Myrtaceae			
Callistemon linearis Bottle bush	Australia	fr	Chico, California
Eucalyptus nephophila Eucalpytus	Australia	le	Glenn Dale, Maryland
Eugenia coronata	South America	le, fl	Coconut Grove, Florida
Eugenia jambos Rose apple	E. Indies	le, fr	Savannah, Georgia
Myrciaria cauliflora Jaboticaba	Brazil	le	Coconut Grove, Florida
Nyssaceae			
Camptotheca acuminata		le	Chico, California
Oleaceae			
Fraxinus chinensis Ash	Central & West China	fr	Glenn Dale, Maryland
Olea europaea Olive	Mediterranean	le	Murrieta, California

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TABLE III (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Tested*	Source of Material Tested
Onagraceae			
Circaea quadrisulcata v. canadensis Enchanters Nightshade	North America	wp	Burtonsville, Maryland
Oenothera biennis Evening primrose	North America	wp, fr	Beltsville, Maryland
Pinaceae			
Larix sp. Tamarack	N. Hemisphere High alt.	le	Glenn Dale, Maryland
Polygonaceae			
Rumex crispus Yellow dock	Europe	ro	Balmorhea, Texas
Eriogonum fasciculatum Eriogonum	W. N. America	le	Ensenada, Mexico
Polypodiaceae			
Polystichum acrostichoides Christmas or Dagger fern	Eastern United States	wp	Burtonsville, Maryland
Punicaceae			
Punica granatum Pomegranate	Persia	le, fr	Chico, California
Rhamnaceae			
Ceanothus sp.	North America	le	Glenn Dale, Maryland
Rhamnus davurica Buckthorn	North China	le	Glenn Dale, Maryland
Rosaceae			
Agrimonia parviflora agrimony	North Temperate Zone	wp	Burtonsville, Maryland
Cerocarpus betuloides		le	Chico, California
Cotoneaster foveolata	Central China	le	Glenn Dale, Maryland
Crataegus azarolus Crataegus Hawthorne	North Africa, Asia	le, fr	Chico, California
Crataegus durobrivensis	North Africa, Asia	fr	Chico, California
Crataegus monogyna	East & North Africa, Asia	le, fr	Chico, California
Malus sieboldii, apple	General	le	Glenn Dale, Maryland
Malus sp. apple	General	le, fr	Glenn Dale, Maryland
Prunus serrulata Flowering cherry	Japan, China	le	Glenn Dale, Maryland
Prunus subhirtella Japanese cherry	Japan	le	Glenn Dale, Maryland
Pyracantha crenulata Fire thorn	Himalayas	le	Glenn Dale, Maryland
Pyrus ussuriensis	Manchuria, N. China	le	Glenn Dale, Maryland
Pyrus calleryana	China	le	Glenn Dale, Maryland

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TABLE III (Continued)

Botanical Name and Common Name if Known	Habitat	Part of Plant Tested*	Source of Material Tested
Rosaceae (Continued)			
Rosa sp. Rose	General	fr	Glenn Dale, Maryland
Rutaceae			
Phellodendron sp. Cork tree	Japan, China	le	Glenn Dale, Maryland
Salicaceae			
Salix nigra Black willow	E. N. America	le, st	Silver Spring, Maryland
Sapindaceae			
Koelreuteria bipinnata	West China	fr	Coconut Grove, Florida
Saxifragaceae			
Deutzia sp.	East Asia	fr	Glenn Dale, Maryland
Hydrangea petiolaris Hydrangea	Japan	le	Glenn Dale, Maryland
Philadelphus henryi, Syringa Mock orange	Asia, N. America	le	Glenn Dale, Maryland
Scorphulariaceae			
Paulownia fortunei	S. E. China	le	Glenn Dale, Maryland
Tamaricaceae			
Tamarix juniperina Tomarick	Japan, N. China	le	Glenn Dale, Maryland
Theaceae			
Franklinia (Gordonia) alatamaha, Franklinia	Georgia	fl	Glenn Dale, Maryland
Ulmaceae			
Zelkova serrata	Japan	le	Beltsville, Maryland
Xyridaceae			
Xyris flexuosa		ro	Southport, N. Carolina

*bu - bulk; fl. - flower; fr - fruit; ib - inflorescent bud; in - inflorescence; le - leaves; rh - rhizomes; st - stems; ro - roots; tu - tubers; tw - twigs; wp - whole plant; (1) young plant, (2) plant in fruit, (3) plant flowering and fruiting.

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Aging Characteristics of Side Leather*

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INTRODUCTION

The inability of some chrome-vegetable retanned side upper leather to withstand storage conditions of high humidity and tropic temperatures has been observed by the Military in storage areas where such conditions prevail.

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Many reasons have been suggested as to the cause of the damage which occurred but have not been proven by actual tests. To determine how other tannages for shoe upper leather would withstand storage under high humidity and tropic temperatures the present work was undertaken.

Prior to World War II it had been established that excessive acidity in vegetable tanned leather lowered its aging stability. This was demonstrated by the work of the National Bureau of Standards in 1925 and reviewed by Bowker and Wallace [1] in 1939. As no specific information was available on chrome-vegetable retanned leather Dudley [2] in 1948 conducted experiments on the effect of retannage on the pH of the leather. From his results he concluded that complex formation occurred between the components of vegetable tannin and the salts present in the basic chrome liquor. The complex formation resulted in the lowering of the pH of chrome liquor-vegetable tannin mixtures. The pH of the chrome liquor was lowered more by hydrolyzable tannins than by condensed tannins.

For an aging test Dudley exposed chrome-vegetable retanned leather to an atmosphere of 100 per cent relative humidity at 40°C. for eight weeks. Tensile strength was used to determine the breakdown due to storage and a significant breakdown was observed.

The effect of para-nitrophenol on the storage stability of chrome-vegetable retanned leather was studied by Lollar [3]. Chrome-vegetable retanned leather was stored for one year under four storage conditions. The leathers were exposed to temperate, desert dry and tropic moist conditions in the Philadelphia Quartermaster Depot Climatization Rooms and to the A.L.C.A. humid storage suggested for the mold resistance test. Based on the strength changes in the leathers the humid A.L.C.A. storage was the most severe. This storage consists of suspending the leather samples over water at 35°C. in sealed glass jars and was similar to the storage conditions used by Dudley except he stored at 40°C. for only eight weeks. The A.L.C.A. storage conditions caused a significant drop in strength as measured by either ball burst or stitch tear strength. A decrease in the pH of the stored leathers was observed whether paranitrophenol was present or not, but the para-nitrophenol lessened the decrease.

In 1954 Wilson, Merrill and Higby [5] reported on six unworn, but badly deteriorated army combat boots, that had been stored in the tropics. The boots were produced in 1944 and 1945 and showed extensive mold growth. Analyses and tests of cuttings from the vamps and quarters of these boots showed a low grease content, low pH values and reduced strength which if the leathers originally met specifications would indicate a considerable decrease.

Experimental

For the study three lots of leather were received from a tanner of side upper leather. One lot of 15 sides was a chrome-vegetable retan leather which was stuffed. A second lot of 15 sides was a straight chrome* tanned leather which had been fat-liquored. The third lot of 15 sides was a straight vegetable tanned leather which had been fatliquored.

Pieces 2 by 8 inches were cut from each side for controls. Immediately adjacent pieces were cut for aging tests. The pieces were aged in chambers at 20°C., 30°C., and 40°C. over water and the chambers were sealed to maintain a high relative humidity. The pieces did not receive any pretreatment and when placed in the chambers were dry.

Condensation of water occurred on the samples suspended above the water level in each chamber in a few days at each temperature. At the end of eight weeks the pieces were removed and tested for ball burst strength. Mold growth was profuse on the vegetable and the chrome tanned leathers but the chrome-vegetable retanned leather which contained para-nitrophenol repelled the mold growth. As the leathers were not completely wetted through and did not show the extended breakdown as observed on smaller specimens previously used, where edge effect allowed for more rapid breakdown, the samples were placed back in the chambers for another eight weeks.

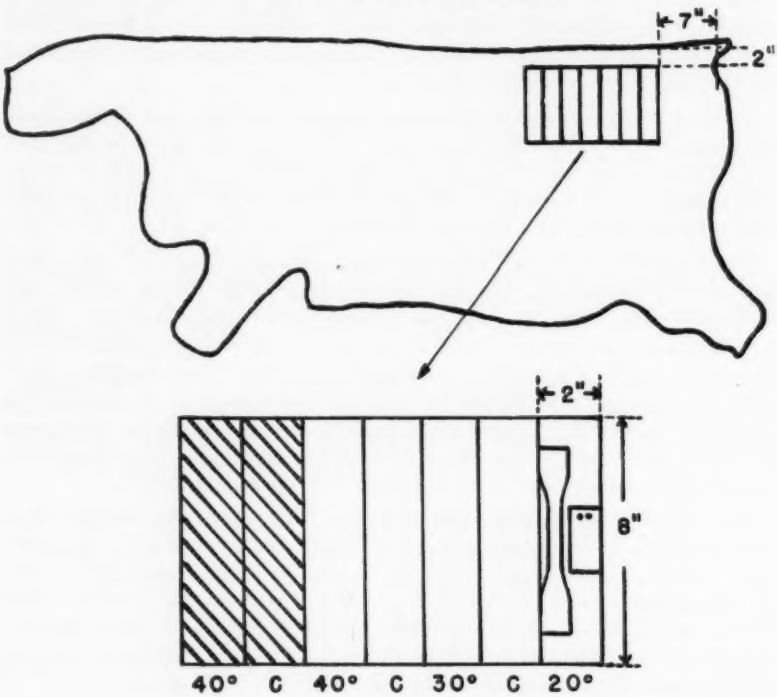
At the end of the second eight weeks (total 16 weeks) the leathers were removed from the aging chambers and tested again for ball burst strength. As there was breakdown on all leathers other physical properties such as tensile strength and stitch tear strength were also determined at this time. The chrome and vegetable tanned leathers after aging for sixteen weeks showed considerable mold growth on each specimen at all three temperatures but the chrome-vegetable retanned leather did not show any mold growth.

Because the chrome and the vegetable tanned fatliquored leathers had mold growth it was felt that the molds might be responsible for the decrease in strength observed in these leathers upon aging. To determine if this was the case the aging test was repeated using merthiolate to prevent mold growth. The specimens were soaked in a merthiolate solution (1-50,000 dilution) for the two hours prior to aging. The specimens were exposed at 40°C. and at a relative humidity of 100 per cent because this set of conditions showed the greatest breakdown in the previous test.

The sampling plan used for cutting the pieces from each of 15 sides, as representative of each tannage, is given in Figure 1. The drawing in Figure 1 shows the arrangement where immediately adjacent pieces are used. The piece from each side aged at 20°C. was taken 7 inches from the root of the tail and 2 inches down from the backbone. The piece was 2 by 8 inches. The rest

*Glucose reduced chrome liquor with no masking agents used.

FIGURE I
SAMPLING PLAN



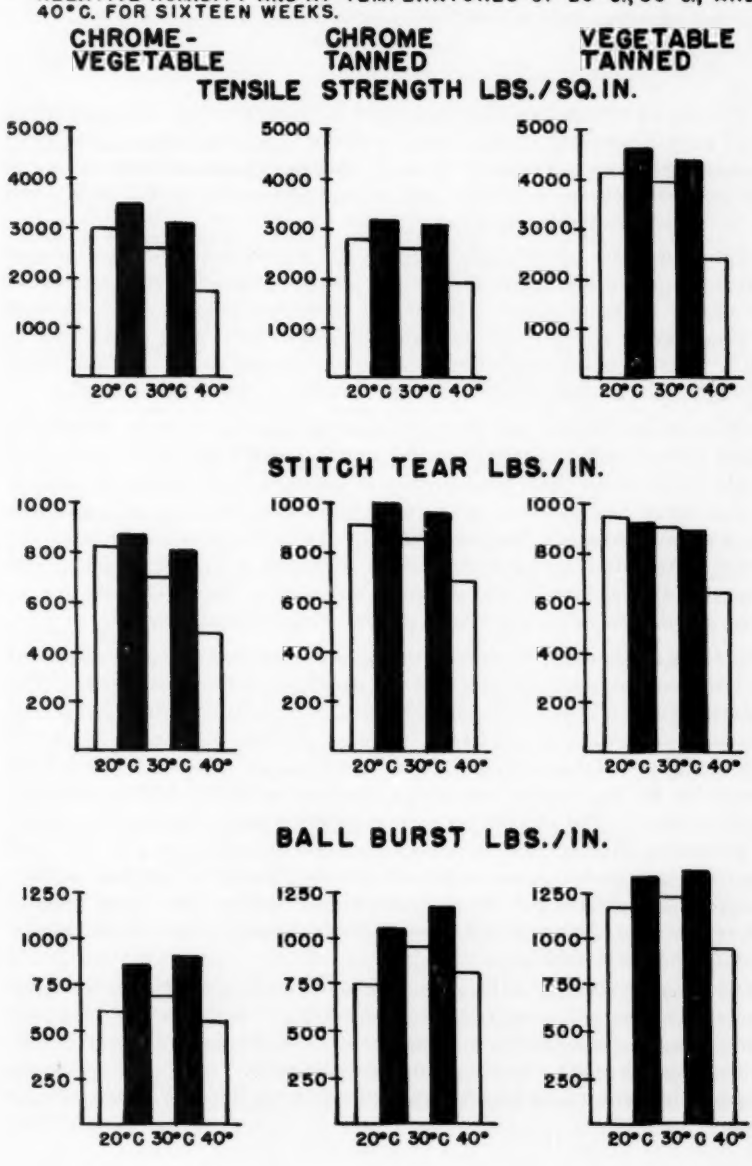
of the pieces were cut immediately adjacent to one another with a control piece dispersed between each piece to be aged.

As shown in the drawing the tensile strength and stitch tear specimens were cut from the control or aged pieces from the center to prevent edge effect. Ball burst strength was determined on the area above the stitch tear specimen. The control pieces were cut for test purposes immediately and after conditioning were tested. The 2 by 8 inch pieces, subjected to the aging were removed from the aging chambers and dried at room temperature for one week. They were then conditioned and ball burst strength determined. The specimens for tensile strength and stitch tear strength were then cut and tested.

The 2 by 8 inch pieces were selected so as to eliminate, as much as possible, the variation in strength from area to area. For the repeat test where merthio-

FIGURE 2

STRENGTH CHANGES OF SIDE LEATHERS EXPOSED AT 100 PER CENT RELATIVE HUMIDITY AND AT TEMPERATURES OF 20°C., 30°C., AND 40°C. FOR SIXTEEN WEEKS.



late was added to prevent mold growth the two pieces shaded in the drawing in Figure 1 were used. The same technique of sampling, drying, conditioning and testing were conducted on these pieces.

Results

The results obtained on the pieces aged for sixteen weeks, and upon which mold growth occurred on the chrome and the vegetable tanned, fatliquored leathers, are given in Figure 2. Strength changes of side leathers exposed at 100 per cent relative humidity and at temperatures of 20°C., 30°C., and 40°C. for sixteen weeks are given.

The white bars labeled 20°, 30°, and 40° represent the temperatures at which the pieces were aged and are the average values for 15 specimens in each case. An examination of the graphs show that aging caused a decrease in almost every strength measurement. The decrease is most pronounced at 40°C. The vegetable tanned leather had the highest tensile and ball burst strength but was similar to the chrome tannage in stitch tear strength.

Chemical analysis of the chrome-vegetable retanned leather which contained para-nitrophenol showed no decrease in grease content but a decrease in pH values at all three temperatures of exposure, as is shown in Table I. In the chrome tanned leather where mold growth occurred during aging there was a definite change in the grease content. As the temperature increased the grease content decreased and the pH also decreased as a result of aging. The vegetable tanned leather also showed a decrease in grease content due to aging accompanied by a decrease in pH at all three temperatures.

As the leathers at 40°C. showed the most pronounced change a statistical analysis was conducted to determine if a significant difference occurred. The results in Table II indicate the change which occurred as a result of aging. For tensile strength there is a marked change for all three tannages. For stitch tear strength the chrome-vegetable retanned leather is down below a level acceptable for shoe upper leather as specified in MIL-L-3122A, Military Specification, [4]. The chrome and the vegetable tanned leathers would still be acceptable although they have decreased in stitch tear strength. The ball burst strength of the chrome-vegetable retanned leather is also low in comparison to the chrome and the vegetable tanned leather after aging. The t-values indicate a significant difference between the control specimens and the aged specimens in each case.

The chrome-vegetable retanned leather seems to be altered more by aging than the chrome or the vegetable tanned leathers. However these leathers also decreased in strength due to aging to a significant extent. As mold growth occurred on the chrome and vegetable tanned leathers their presence could be associated with the change in strength which occurred in these two tannages.

TABLE I

Chemical Analyses of Leathers Exposed at 100 Per Cent Relative Humidity and at Temperatures of 20°C., 30°C., and 40°C. for Sixteen Weeks.

	Chrome-Vegetable Retan Leather				
	Control 2	Control 4	20°C. 1	30°C. 3	40°C. 5
Moisture %	13.89	14.39	13.32	12.88	12.71
Grease % (Moisture Free Basis)	22.96	23.19	22.41	22.22	23.73
Hide Substance % (Moisture Free Basis)	51.76	52.30	50.62	50.53	50.74
Total Ash % (Moisture Free Basis	4.08	4.23	3.95	3.99	3.86
Chrome % (Moisture Free Basis)	3.46	3.30	3.29	3.30	3.19
Chrome % (Hide Substance Basis)	6.68	6.31	6.50	6.53	6.29
pH	3.08	3.07	2.90	2.95	2.94
Water Solubles % (Moisture Free Basis)	1.01	1.01	0.85	0.65	0.80
Insoluble Ash % (Moisture Free Basis)	3.97	3.99	3.91	3.97	3.84
Vegetable Tannin % (Moisture Free Basis)	21.20	20.28	23.02	23.26	21.67
Paranitrophenol %	0.29	0.29	0.25	0.24	0.20
	Chrome Tanned Leather				
	Control 2	Control 4	20°C. 1	30°C. 3	40°C. 5
Moisture %	16.83	16.91	14.34	14.46	15.03
Grease % (Moisture Free Basis)	8.68	9.05	4.53	7.38	2.26
Hide Substance % (Moisture Free Basis)	76.50	76.00	75.48	73.98	78.32
Total Ash % (Moisture Free Basis)	6.02	5.95	5.74	5.74	5.98
Chrome % (Moisture Free Basis)	4.67	4.84	4.74	4.67	4.89
Chrome % (Hide Substance Basis)	6.10	6.37	6.28	6.31	6.24
pH	3.63	3.62	3.28	3.18	3.04
	Vegetable Tanned Leather				
	Control 2	Control 4	20°C. 1	30°C. 3	40°C. 5
Moisture %	13.70	13.44	11.51	11.45	11.73
Grease % (Moisture Free Basis)	12.93	13.93	9.40	8.94	6.79
Hide Substance % (Moisture Free Basis)	56.30	56.30	56.35	56.12	56.86
Total Ash % (Moisture Free Basis)	0.82	0.85	0.81	0.82	0.88
pH	4.45	4.45	3.46	3.23	3.30
Water Solubles % (Moisture Free Basis)	3.86	3.85	4.49	5.57	5.37
Insoluble Ash % (Moisture Free Basis)	0.58	0.57	0.45	0.41	0.41
Combined Tannin % (Moisture Free Basis)	26.33	25.35	29.31	28.96	20.57
Degree of Tannage (Moisture Free Basis)	46.77	45.03	52.01	51.60	53.76

When merthiolate was added to the leathers to prevent mold growth and the specimens aged for 16 weeks the results given in Table III were obtained. Examination of the strength values of the chrome-vegetable retanned leather shows low stitch tear strength and low grain crack strength. The chrome leather while decreasing somewhat in strength has a higher average tensile strength and stitch tear strength than observed when mold growth occurred. The vegetable leather also has higher average tensile strength and stitch tear strength than observed when mold growth occurred. The t-values again indicate a significant difference between the control specimens and the aged specimens.

TABLE II

Strength Changes of Side Leathers Exposed at 100 Per Cent Relative Humidity and at a Temperature of 40°C. for Sixteen Weeks.

Strength Measurements	Chrome-Vegetable Retan	Chrome Tanned	Vegetable Tanned
Tensile Strength Lbs./Sq. In.			
Control	3296	3096	4416
Aged At 40°C.	1871	1950	2433
t Value	10.8	5.9	8.4
Stitch Tear Lbs./In.			
Control	806	979	893
Aged At 40°C.	474	681	644
t Value	11.7	5.1	7.1
Ball Burst Lbs./In.			
Control	844	1155	1342
Aged At 40°C.	535	822	963
t Value	9.0	3.9	6.3

99 % SIGNIFICANT VALUE t = 2.76
99.9% SIGNIFICANT VALUE t = 3.67

TABLE III

Strength Changes of Side Leathers Exposed at 100 Per Cent Relative Humidity and at a Temperature of 40°C. for Sixteen Weeks. Merthiolate Added to Prevent Mold Growth.

Strength Measurements	Chrome-Vegetable Retan	Chrome Tanned	Vegetable Tanned
Tensile Strength Lbs./Sq. In.			
Control	3683	3532	3916
Aged at 40°C.	1855	2573	3297
t Value	9.8	4.5	3.1
Stitch Tear Lbs./In.			
Control	895	1039	1083
Aged at 40°C.	470	881	710
t Value	10.2	3.5	11.4
Ball Burst Lbs./In.			
Control	836	933	1521
Aged at 40°C.	390	676	965
t Value	15.1	4.8	8.2

99 % SIGNIFICANT VALUE t = 2.76
99.9% SIGNIFICANT VALUE t = 3.67

Chemical analyses of the leathers are given in Table IV. The merthiolate not only prevented mold growth from occurring on the chrome and the vegetable tanned leathers but also prevented a decrease in grease content and a marked decrease in pH.

The chemical data reported do not show the extent of the hydrolysis which occurs as well as the strength measurements do. The chemical analyses do show that even when mold growth did not occur the pH of the leather still decreased as a result of aging. There may be a reversal of the tannage during aging but the analytical techniques used did not indicate a reversal taking place. However it is possible to have the same amount of tannin present but oriented in a different manner which results in a decrease in strength.

TABLE IV

Chemical Analyses of Leathers Exposed at 100 Per Cent Relative Humidity and at a Temperature of 40°C. for Sixteen Weeks. Merthiolate Added to Prevent Mold Growth.

	Chrome-Vegetable Retan Leather Control	40°C.
Moisture %	10.18	10.09
Grease % (Moisture Free Basis)	24.20	22.94
Hide Substance % (Moisture Free Basis)	49.19	50.79
Total Ash % (Moisture Free Basis)	3.83	3.89
Chrome % (Moisture Free Basis)	2.78	3.24
Chrome % (Hide Substance Basis)	5.65	6.38
pH	3.13	2.90
Water Solubles % (Moisture Free Basis)	0.48	0.69
Insoluble Ash % (Moisture Free Basis)	3.75	3.81
Vegetable Tannin % (Moisture Free Basis)	22.38	21.79
Paranitrophenol %	0.29	0.17
	Chrome Tanned Leather Control	40°C.
Moisture %	12.68	12.28
Grease % (Moisture Free Basis)	7.93	6.75
Hide Substance % (Moisture Free Basis)	73.77	75.53
Total Ash % (Moisture Free Basis)	5.85	5.54
Chrome % (Moisture Free Basis)	3.98	4.63
Chrome % (Hide Substance Basis)	5.40	6.13
pH	3.63	3.40
	Vegetable Tanned Leather Control	40°C.
Moisture %	10.11	9.23
Grease % (Moisture Free Basis)	13.20	12.04
Hide Substance % (Moisture Free Basis)	54.98	55.69
Total Ash % (Moisture Free Basis)	0.90	0.64
pH	4.44	4.15
Water Solubles % (Moisture Free Basis)	3.45	1.47
Insoluble Ash % (Moisture Free Basis)	0.53	0.56
Combined Tannin % (Moisture Free Basis)	27.84	20.24
Degree of Tannage (Moisture Free Basis)	50.64	54.30

Summary

Chrome-vegetable retanned leather which was stuffed with stuffing grease shows the greatest breakdown when aged at 100 per cent relative humidity

and at 40°C. Straight chrome and straight vegetable tannages which were fatliquored also showed breakdown under the same conditions of test but the breakdown is not as severe.

Breakdown occurs whether mold growth occurs or does not grow on the leather during aging. A decrease in grease content due to aging is not the main factor in decrease in strength because if the grease content of the leather is not altered by aging the strength of the leather still decreases.

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Discussion

W. R. Lotz: I appreciate the opportunity to thank Bill Roddy for this paper and also to express my appreciation to the group for allowing a tanner to comment upon something which is near and dear to his heart, that is, leather.

In going over this paper with Bill, one of the things I was struck by as a tanner, was the non-definition in the paper of the manufacture of the leather involved.

After some discussion I found that in all fairness we should define those leathers. These leathers were not made, for example—if you are discussing the Army retanning phase of this paper—these leathers were not made by one who is normally making Army retan. In the case of all three leathers they were made by one tanner who normally makes and is noted for a vegetable type tannage. I would like to call that to the attention of the members in connection with this paper.

I was also intrigued, in studying the data presented, in trying to determine whether the tannage as such was a masked chrome tannage, and also whether the materials like formates were used in connection with the tannage because work previously done has indicated some particular benefit through the use of formates, especially on Army retan, in protecting the particular type of leather against deterioration.

In the paper reference was made to a report by Wilson, Merrill and Higby, on retans of Army boots in which they reported a low grease content, low pH and reduced strength based on the fact that "leather should have met specifications in 1944 and 1945." I do not believe that these are valid conclusions because those who have had some experience with the manufacture of Army type leathers during the years 1944 and 1945 know that many new tanners began to make Army retan and that the Army laboratories were way behind in analysis and that shoes were made and shipped before analysis came through.

And much sub-standard leather was accepted in Army shoes by the Army, but with penalties to the tanners, or the shoe manufacturers. Also in the case of this particular report, I do not believe there was any particular way of identifying the manufacturers of the leather and the leather in the shoes may have been from a very acid tanned leather coming out of the tannery at a pH of 2.6 or 2.7 and with original low grease contents.

Incidentally, one of the important things in this particular report of Bill Roddy's is that his report does not confirm a decrease in grease content.

In studying the data—and I am sorry a lot of the data was not presented—one of the things that struck me—and I hope that you will read the data—and which I would like to ask Bill about, is about the moisture control.

Since this is a paper on humidity and the effect of water—one must note that the degree of moisture in the control samples was higher than that of the test samples.

For example, on chrome-vegetable retanned, the control samples were 14 and 14.4. This is high. Most Army retanned today is being shipped at moisture contents of eight to ten per cent. The samples used, at 20 and 30 and 40 degrees, had moisture contents of 13.3, 12.9 and 12.7.

On the chrome tanned leather, the moisture content of the control was 16.8, and 16.9. These are extraordinarily high control samples as far as moisture is concerned. In the samples under test the figures were 14.3, 14.5 and 15.

On the vegetable tanned leather, the control samples were 13.7 and 13.4; and in the tests they were 11.5, 11.5 and 11.7.

Also, in studying the data, it became evident that the pH indicated an acid tannage, that is, a tannage not masked with formate.

And in the Army retan type leather, the thing that leads me to suspect that the man who made the leather did not know a great deal about Army retan, the level of chrome was extraordinarily high, and would indicate a person who made the leather by a high chrome over-tannage before he put on the vegetable, or one who originally put in a small amount of chrome, a great deal of vegetable, and then came back over with chrome.

On the study of the data on the chrome and vegetable, again we find that the moisture controls were higher than the test samples and also we had a

great decrease in grease. And again the pH indicated an unmasked tannage.

Incidentally, in the merthiolate series the moisture in this test did not coincide by three or four per cent with those in the original test. I think there may have been some difficulty with the storage conditions.

I would also have appreciated having had one other piece of data presented (if you don't mind this comment) that is, if included with the data there had been some data on a chrome-vegetable fatliquored leather, a leather which many tanners in the United States make today. There was a chrome-vegetable stuffed, a chrome fatliquored, a vegetable fatliquored, but I would have liked to have seen data on a chrome-vegetable fatliquored leather compared to the other three types of tannages and retannages.

I would like for a few minutes to ask Bill Roddy to comment on some of these points I have brought up. Can you tell us a little about the tannage involved in these tests?

W. T. Roddy: I have been assured by Dr. O'Flaherty—and I was fairly sure before—that it was actually a chrome tannage first followed by a vegetable retannage, which is partly an answer to Bob's question.

However, in regard to this chrome retanned leather, it would meet, even at the present time, the Federal specifications for Army size upper leather based on the chemical analysis.

In regard to a low pH, as an example, there was a pH of 3.08, which is still acceptable as far as pH for Army side upper leather is concerned.

Bob Lollar in his work on the para-nitrophenol used some seven different tanners' chrome-vegetable retanned side upper leathers. And on the basis of chemical analysis, these met the Government specifications and still showed a decrease in ball burst strength and stitch tear strength.

As to whether the chrome liquor used by the tanner was a glucose reduced or formate masked liquor, I do not know; I was under the impression it was a glucose reduced liquor without formate added. But I am not certain of that.

The next point to which I would like to call to your attention is of the question that, as Bob pointed out, the chemical data in regard to a decrease in grease content is not borne out by the results which we have. I have the figures here. As an example, for the chrome-vegetable retanned leather there was no decrease in grease content because of the paranitrophenol. The chrome tanned specimens had a grease content of 9.05. After exposure at 20 degrees Centigrade we came up with 7.38; and at 40 degrees it was 2.26, which is certainly a reduction in grease content from the standpoint of the chrome tanned specimens.

For the vegetable tanned leather, on controlled samples, it was 13.93. After exposure at 20 degrees Centigrade it was 9.40; at 30 degrees, 8.94; and at 40 degrees, it was 6.79. So that is certainly a reduction in grease content.

Of course on the repeat experiment, where we used merthiolate on the chrome and vegetable tanned leather it did not result in decreased grease content under those circumstances, but it did result in a lowering of the pH.

In regard to the moisture content, I would like to mention this: as I pointed out in the paper, we tested the control specimens of the leathers immediately. And then in regard to the specimens in the repeat test, they were taken at a later date after being stored in the laboratory for quite a period of time; and even though we put them in the conditioning room and gave them the standard 48 hours of conditioning, they apparently did not come back to the moisture content that Bob is normally used to seeing, but nevertheless they are acceptable.

LOTZ: One more question: in going over the pH data, on the chrome-vegetable Army retanned, the control was at 3.08 and you point out a decrease in pH from 3.08 as follows: at 20 degrees Centigrade it was 2.9; at 30 degrees it was 2.95; and at 40 degrees it was 2.94. This is on the chrome-vegetable stuffed leather.

On the chrome tanned leather, the pH was 3.62, and then at 20 degrees it was 3.28; at 30 degrees it was 3.18; and at 40 degrees it was 3.04.

On the vegetable tanned leather the pH of the control was 4.45; and then at 20 degrees it was 3.46; at 30 degrees, 3.23; and at 40 degrees, 3.30.

There seems to be a considerable more decrease in pH on both the chrome and vegetable leathers than on the chrome-vegetable retanned stuffed leather. Do you care to comment?

RODDY: Do you have a point on that, Seymour?

S. S. KREMEN: You cannot compare a decrease in pH from 4 to 3 and say it is of the same magnitude as a decrease from 3 to 2. Because the pH is a logarithmic function, the decrease from 3 to 2 includes the formation of 10 times as much actual acid.

LOTZ: But there is also another point here. A lot of Army retanned leather is brought out at a much higher pH than that indicated here. 3.08 is acceptable but you typed values in pH of Army retanned leather considerably higher and I do not believe you will find the decrease in pH as great on those leathers at 3.4 and 3.5 than you will at 3.0.

RODDY: I cannot offhand remember the analytical data we obtained on the seven tannages used by Bob Lollar which were exposed for a period of a year under various conditions mentioned briefly, but I would say that there was a fair range of pH and I would anticipate, if my memory serves me, that it went probably from 3½ down to 3 on the seven tannages.

R. M. LOLLAR: That is what I was going to comment on. This leather which, while it was not made by a tanner accustomed to make the tannage, was within the range of those leathers which were submitted to us by those tanners who were making that leather.

Furthermore, retanned leather made by those customarily making retanned leather, has shown a phenomenon which is this:—(It may not be a property of the leather although it most logically is.)—When the leather was received it was tested immediately. Then, after one year of aging in the Philadelphia Quartermaster Depot, at the climatic conditions simulating United States exposure in the mid-south, Memphis area, it was again tested. We find that it did not retain, even under those relatively mild storage conditions, the properties that it had at the start of that year's storage when it was fresh leather.

I say that with some qualification because in any test of a year's holding you have the problem of the reproducibility of the testing machines and the operators involved. It is my feeling, and this will have to be confirmed by more experimentation, that this is not a property of the testing machine and the operators involved, but a property of the leather. There is a phenomenon which is accelerated by these results at 40, but which goes on as these results show, at 20, and at less humid test conditions than any of these results show.

J. R. KANAGY (National Bureau of Standards): We have done some work which indicates that a high grease content causes deterioration of a chrome retanned leather. So before you finish your work it might be pertinent for you to study this point and see if that is the reason that this particular chrome retanned leather shows such a high degree of deterioration.

RODDY: It is not only this one, but that point was brought up by Bob Lotz: that a chrome retanned fatliquored should preferably be used. What we are investigating in this case and have over a few years, is trying to find the exact mechanism for this breakdown in the chrome-vegetable combination tannage. And back when we began the work it was made with a grease content of from 25 per cent up to as high as 35 per cent. That is when we started.

C. W. MANN: I think there has been some interpretation of this as being more or less of a non-standard type of leather. There have been some questions regarding this particular leather. Maybe the results you are getting are due to the fact that you have an abnormal type of leather.

However, our aging tests in the Quartermaster chambers have included more than a hundred lots of leather from a dozen different tanners and results that we have been finding on chrome retanned leather correspond to yours. They show that the chrome retanned leather under this more or less tropical type of condition does not stand up as well as either the vegetable or the straight chrome tanned leather.

I think also the indirect evidence we have from a study of several hundred pairs of shoes, returned from the Southwest Pacific, that had not been worn and had remained in the storage cases in which they were shipped overseas—comparing results on the strength of those leathers with the strengths we are getting in our storage chambers, in which we are protecting the leather from mold, also confirm the results you find here—that there is a deterioration process that goes on independently of the mold, but the process that goes on in the presence of the mold is two times, or more than that, as great as the one that goes on in the absence of mold.

All of the leathers we have stored in the Quartermaster storage chambers have been treated with paranitrates and are therefore protected from mold growth. I think the rates of deterioration you are getting at 40 degrees Centigrade are greater than we are getting under our storage conditions, which is what should be expected. Also from the differences you are getting between the chrome and vegetable and the combination tanned leather, I believe the difference you are getting is somewhat greater too than the difference we get in the storage chamber. However, the relative rating of storage is the same as you have in your test.

KREMEN: One of the insole leathers which I discussed in the previous paper, a chrome-vegetable insole leather which showed the most deterioration, was essentially a side leather tannage and the grease content was a little over 4 per cent, fatliquored. That was practically the same as a side leather, except it was not split to a side leather thickness. The same low resistance to deterioration was noted thereto.

ABSTRACTS

A Critical Review of the Literature of 1953 — (Tannery Wastes). By H. Heukelekian, (Chairman). *Sew. and Ind. Wastes*, **6,** 695 (1954). Included in the review of Industrial Waste literature is the following on Tannery Waste: "Jung ["Treatment of Waste Waters from Textile and Leather Industries". *Gesundh. Ing.*, **72,** 290 (1951)] reports that tanning wastes can be treated by the Niers process or by the addition of iron salts to the activated sludge process. Coin *et al* ["A Common Method of Treatment for Removal of Cyanides from Galvanizing Waste Waters and of Sulphides from Tanneries Waste Waters". *Tech. Eau (Brussels)*, **6,** 17 (1952)] points out that the destruction of hydrogen sulfide in caustic tanning wastes can be obtained by aeration at great saving in cost of aeration if the wastes are first acidified. They state that the cost of operation of the process is about one-third of that for chlorination. Stundl ["Damage to Streams by Tannery Waste Waters". *Ost.* Wasserw., **3,** 100 (1951); *Water Poll. Abs.*, **26,** 493 (1953)] indicates that tanning wastes may contain substances that will inhibit the growth of organisms that decompose the organics in these wastes. Iyer *et al* ["Soil Conditions as Affected by Tannery Waste Waters". *Quart. Jour. Indian*

Inst. Sci., **34**, 2 (1952)] state that agricultural land adjoining an area where waste waters from a tannery were impounded became infertile. The general principles applicable to the treatment of tannery wastes, the composition of these wastes, and the equipment for the disposal of the liquids from a typical heavy leather tannery using the vegetable tan process are given by Redlich ["Problem of Tannery Waste Disposal". *Jour. Amer. Leather Chem. Assn.*, **48**, 422 (July 1953).] Hartman ["Treatment of Tannery Wastes and Domestic Sewage at Fond du Lac, Wis." *Sew.* and *Ind. Wastes*, **25**, 1419 (Dec. 1953)] indicates the necessary pretreatment that is needed if tannery wastes are to be treated with municipal sewage". J.F.W.

Trade Effluent Treatment with Aluminoferric. By J. H. Harwood. Reprint from *Ind. Chem.* (July, 1953) through *Sew.* and *Ind. Wastes*, **26**, 812 (1954). The author discusses the treatment of effluents, the types of plants used, and the results obtained with the coagulant aluminoferric on various industrial wastes (23 plants), from a British standpoint. Reductions in oxygen absorbed and suspended solids are noted, although coagulant treatment by itself is generally only satisfactory if the effluent is discharged to a municipal sewer. Tannery wastes are the hardest to treat. On domestic sewage, the use of the coagulant has been helpful in improving settlement and reducing the load on filters.

Treatment of Tannery Waste and Domestic Sewage at Fond Du Lac, Wisconsin. By B. J. Hartman. *Sew and Ind. Wastes*, **25**, 1419 (1953). Fond Du Lac was one of the first cities of Wisconsin to construct a plant for the treatment of domestic sewage. In the late 1800's an Imhoff tank was constructed and with many modifications and improvements was operated until the early 1920's. By then it had become entirely inadequate and was replaced by a new plant of the separate sludge digestion type, consisting of two clarifiers, two digesters, and sludge beds. Little or no consideration was given to the treatment of wastes from the tannery or dairy products plants. These industries continued to discharge their wastes into the Fond Du Lac river until the late 1920s. Based on studies and recommendations made by the Wisconsin State Board of Health during 1929, two additional clarifiers for the pretreatment of tannery waste were constructed adjacent to the clarifiers handling the domestic sewage. The tannery waste was pumped through a force main directly to those clarifiers. The original plan was to discharge the effluent from the tannery clarifiers into the influent of the domestic clarifiers, resulting in the treatment of the combined waste in the domestic clarifiers. In practice it was found that the tannery clarifiers did an excellent job of removing suspended solids and little could be gained by further settling. Therefore, the practice was discontinued. An attempt to digest tannery sludge with domesting sludge met with little or no success, probably because of insufficient digester capacity. Sludge from the domestic clarifiers was pumped to the digesters, which functioned more or less satisfactorily. Sludge from the tannery clarifiers was pumped to nearby lagoons until lack of space and the obnoxious odors necessitated a change. Based on an investigation and study completed in 1945 the following recommendations were made: 1. The pumping station necessary to pump the sewage through the disposal plant be made a part of the disposal plant instead of a separate unit approximately 1500 ft. from the plant. 2. A drum-type screen be included in the treatment plant to screen the tannery waste before combining it with the domestic sewage. 3. The plant pumping station have a capacity of 25 m.g.d., with the pumps operated by electric motors and sludge gas engines. The plant include the following units, the flow passing through these units in the order named: (a) Meters for both domestic and tannery sludge. (b) Grit removal equipment, the tannery waste being mixed the domestic waste just ahead of this unit.

(c) Flocculator. (d) Primary clarifiers. (e) Rock filters for operation as either standard or high rate filters. (f) Final clarifiers. (g) Digesters. (h) Vacuum filters and flash drying equipment to condition the sludge for disposal. The plant was designed for an ultimate dry-weather flow of 8 m.g.d and a B.O.D. of 12,900 lb., equal to a population equivalent of 77,000 (Fond Du Lac has a population of 30,000; 1950 census). At that time it was estimated that the domestic sewage, including that from two dairy plants, would be 4.5 m.g.d. and the tannery flow 1 m.g.d. Because it was anticipated that a considerable volume of storm water would reach the plant, provisions were made to handle a total flow of approximately 25 m.g.d. The pumping capacity at the plant at the designed head is 21.5 m.g.d., but with a reduction of 5 ft. in head during storm flows this capacity is increased to 25 m.g.d. The grit removal equipment and flocculator have a rated capacity of 20 m.g.d. The balance of the units can be operated at a 20 m.g.d. rate, but since this exceeds the designed capacity the efficiency would be reduced. The sludge from the primary clarifiers is pumped to the digesters while sludge from the final clarifier is pumped to the primary clarifier for settling and mixing with primary sludge. The pumping equipment is so arranged that it is possible to pump final clarifier or filter effluent to the rock filters in order that high dosing rates can be maintained. The four clarifiers of the primary treatment plant were all converted to digesters. This resulted in six digesters, each 50 ft. square and 17.5 ft. deep, having a total digester volume of 262,500 cu. ft. Four of the digesters have fixed covers with stirring mechanism and are considered primary digesters; two are considered final digesters, having floating gas holders with a gas storage capacity of approximately 15,000 cu. ft. each. The sludge is heated by hot water coils in the digesters and a 500,000 B.t.u. per hour external sludge heater using either sludge gas or fuel oil. The sludge is drawn from the final digester to two vacuum filters each 6 ft. in diameter by 8 ft. long, which reduce the moisture from approximately 96 per cent to approximately 70 per cent at a rate of 3 lb. per sq. ft. per hr. The moisture content is further reduced to approximately 20 per cent by flash drying equipment. The dried sludge is bagged and sold for fertilizer. A garbage and refuse incinerator having a capacity of 90 tons per 24 hrs., together with the necessary truck storage was also included in the design. This unit was so arranged that the waste heat from the incinerator can be used for sludge drying or the sludge can be incinerated.

The plant was put into operation in 1950 and from the plant operating records it is apparent that quite good and consistant results are being obtained. In July 1952 the Wisconsin State Board of Health ran a 24 hr. test and from the results, which can be considered as representative, an over-all reduction in B.O.D. of 90 per cent was indicated and an over-all reduction in suspended solids of 92 per cent. During 1953 a total of 1,740 tons of sludge was dried, or approximately 6 tons per operating day. The dried sludge is bagged and sold at $5.50 per ton; this assists materially in reducing the plant operating costs. The amount of gas produced has varied from 45,000 to 60,000 cu. ft. per day and with certain improvements higher yields are anticipated. Consideration is now being given to the installation of equipment for the generation of electric power and the reclaiming of heat. Preliminary estimates indicate that the value of useable power and heat will amortize the required investment in somewhat less than 10 years. J.F.W.

The Influence of "Breaking Over" Sun Dried Sheepskins During Soaking on Water Uptake. G. H. Green. *J. Soc. Leather Trades' Chemists*, **38**, 198 (1954). Sun dried sheepskins are stretched during soaking. The term applied to this operation is "breaking over". It is thought that the water uptake after this treatment is greater, thus reducing soaking time. This experiment was undertaken to obtain evidence in support of this belief. Five different types of sheepskins were tested. The skins were soaked until the

rate of water uptake had become very low or ceased (3-4 days), and were then broken over and resoaked. There was no immediate increase in the water uptake, but usually there was an appreciable amount taken up in the next 24 hours, after which water content remained constant or decreased. If the skins were broken over after only one day's soaking i.e. before attaining maximum water uptake, the maximum uptake was reached in 3-4 days in contrast to 4-5 days, if breaking over was delayed until after maximum uptake was accomplished. Also, in 4 out of 5 skins, early breaking over gave a greater final uptake than for the same skins with delayed break over. Over soaking decreased water content regardless of the time of break over. However the tensile strength of the undersoaked skin is less than that of the fully soaked. Hence early breaking over may promote tearing. The conclusion was reached, therefore, that the period of soaking prior to breaking over should be just sufficient for the skin to reach its maximum water uptake and mechanical strength, but not long enough for bacterial action to become apparent. The skins should then be broken over and passed on to the next process. If further soaking is necessary, it should be restricted to one day. If, in times of emergency, the time of soaking is increased, an antiseptic should be added to the water. The assessment of the most suitable soaking time is usually left to personal experience, since it is dependent upon two factors, the temperature of the soak water and the variety of skin. The temperature used for these experiments was 50-56° F. It should be noted that any bacterial attack which takes place during soaking cannot be ignored even in the sweating process. Soak waters are anaerobic whereas the bacteria active during sweating are areobic. The anaerobic bacteria in soak water can loosen the wool, but only at the expense of deep seated putrefaction.

R.H.T.

Determination of Functional Groups in Tannins and Lignins. Part II. Methylation Studies. W. E. Hillis. *J. Soc. Leather Trades' Chemists,* **38,** 209 (1954). It is generally considered that diazomethane will methylate only hydroxyl groups of acidic nature, i.e. carboxylic, phenolic and enolic hydroxyls. The author presents a brief critical review of this assumption, pointing out possible variations and exceptions. Samples of catechin A, aromadendrin and methanol lignin were prepared as in Part I [J.S.L.T.C. **38,** 177 (1954)]. Diazomethane prepared from N-nitroso-beta-methyl-aminoiso-butyl methyl ketone and estimated with benzoic acid, purified methanol and ether of anesthetic grade distilled over sodium were used. Methylation of the lignin and determination of the methoxyl group by the method of Vieböck and Brecher, slightly modified, are described. A study of methylation of aromadendrin and catechin A, using dioxane, dioxane plus 5 per cent water, methanol and ether as solvents was made. Ether proved the best. Also it was the only successful solvent for the methylation of lignin. Hence it was used for subsequent study despite the fact that lignin is insoluable in it. The effect of methylating lignin with diazomethane may be seen in the following table. Two lots of four times the theoretical amount of diazomethane were used; methylated 4 days; product soluable in 2 *N* NaOH at 70° C.; nitrogen absent in methylated products.

Extraction	Original OCH_3 %	Ether Insoluble Fraction % of total recovery	Ether Insoluble Fraction OCH_3 %	Ether Soluble Fraction % of total recovery	Ether Soluble Fraction OCH_3 %	Calculated OCH_3 % in mixture
4 hr.	24.0	71.1	31.3	28.9	32.4	31.6
1st 16 hr.	28.5	69.5	32.2	30.5	34.7	32.9
2nd 16 hr.	28.9	70.3	32.7	29.7	35.7	33.6
3rd 16 hr.	28.6	81.5	32.5	18.5	34.7	32.9

The following conclusions are made. The concept that diazomethane will methylate always

and only hydroxyl groups of acidic nature is shown to be unreliable. The use of alkali during methylation is inadvisable as the methylated products may be ruptured and new phenolic hydroxyls realeased. Methylation studies on aromadendrin (dihydrokaempferol), catechin and lignin showed that the choice of solvents can play a part during methylation with diazomethane. In addition the relative solubilities of the components of lignin were changed during methylation so that purification to a constant methoxyl figure, in the usual manner, would give values of no relationship to the original material. R.H.T.

Tannins VI. Further Examination of Fractions of Quebracho Tannin Extract. K. S. Kirby and T. White *J. Soc. Leather Trades' Chemists*, **38,** 215 (1954). The six main fractions of quebracho extract (Q111, Q112, Q121, Q122, Q21, Q22) described in a previous publication [*J.S.L.T.C.* **37,** 283 (1953) and *This Jour* **49,** 312 (1954)] and obtained by solvent fractionation, have been further examined by counter current solvent distribution and by column chromatography. A nine tube distribution, in a methyl ethyl ketone/water system was used, except for Q111, where a tenth tube with an aqueaous phase of 1 percent acetic acid saturated with methyl ethyl ketone was added. By chromatographing the contents of each tube 2-ways on paper and developing the spots with ferric chloride/ferric cyanide reagent, approximately 25 minor compounds can be observed in addition to those listed in the previous paper. Sugars were present in tubes 8 and 9, except in the case of Q22, where phenolic substances predominate. Sugars indentified were rhamnose, xylose, arabinose and glucose. Fifty-three percent of the water soluble tannins in the whole extract are present in Q111 and Q112. The second fraction of each of these was rechromatographed and the product analyzed for tannin content. Both were methylated and the methylated product acetylated. The analytical results are given below.

	Tans	OCH_3 (methylated)	$[\alpha]_D$ (methylated)	M. W. (methylated)	Acetyl (acetylated methylated)
Q111/2	93.5%	23.9%	32.1°	840	9.9%
Q112/2	94.9%	25.4%	18.7°	866	10.98%

The results show that aliphatic as well as phenolic hydroxyl groups are present; and, in spite of high tannin content, molecular weights are low. All six fractions were acetylated with pyridine and acetic anhydride and the acetylated product (except Q22 which was insoluble in the acetylating mixture) further treated with acetyl chloride and dimethyl aniline. Acetyl analyses of the acetylated fractions were as follows.

Fraction	Acetylation I	Acetylation II
Q111	39.26	39.24
Q112	38.96	38.82
Q121	38.05	38.77
Q122	36.82	37.46
Q21	38.80	38.31
Q22	38.16	----

Examination of the ultra violet spectra of the acetylated fractions showed that about half the phenolic nuclei in quebracho tannins have their hydroxyls free and available for acetylation, while the remainder have their oxygen atoms bound in the ether form and cannot therefore be acetylated. Experimental procedures are given in detail. R.H.T.

Vegetable Tanning VIII. The Properties of Babul Bark (*Acacia Arabica*). D. Burton and S. K. Barat. *J. Soc. Leather Trades' Chemists*, **38,** 223 (1954.). This is a report on the nature of the tannins and tanning properties of babul bark, which grows in profusion in the forests of India. It is compared with myrabalans and mimosa. Babul bark is a catechol tanning material which gives a leach liquor with a comparatively low tan/nontan ration, a high pH and a high salt content consisting mainly of salts of weak acids. It can be used to produce well tanned, harsh, firm, dark brown leather of good tensile strength. The quality would be improved by using a blend with a pyrogallol tanning material such as myrobalans. R.H.T.

Note on Co-ordination of Acid Groups to Chromium. S. G. Shuttleworth. *J. Soc. Leather Trades' Chemists*, **38,** 232 (1954). While there is harmony of viewpoints in previous publications by the author and parallel work carried out by Kuntzel and his coworkers, there is one point of difference. This is in the instantaneous reaction between a solution of sodium acetate and a solution of chromium chloride. These workers, noting the immediate change of color produced, have concluded that the free acid formed by the reaction is attached by hydrogen bonds to the chromium complex. The author's contention is that the change of color is due to very rapid pH and olation changes, that the acetate ion present represses the ionization of the acetic acid and thus the conductimetric titration curve does not show the presence of this free acid. Its presence can, however, be demonstrated by ether extraction. R.H.T.

Oak Bark Tannage: Effects of Variations in Layering. W. E. Braybooks and R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **38,** 233 (1954). The objectives of the experiments described were to get comparisons between layer treatments of 5 and 10 months respectively, and between dustings with oak bark and a mixture of oak bark and valonia. The experimental layerings were of four types as follows: (a) 2½ months in first layer, 2½ months in second. Dust additions in first layer, 3½ lb. oak bark and 3½ lb. valonia per butt; a similar dust addition in the second layer. (b) 5 months in first layer and 5 months in second. Dust additions as in (a). (c) Times in layers as in (a). Dust additions of 7 lb. of oak bark per butt as each layer was laid down. (d) Times in layers as in (b). Dust additions as in (c). The description of the experiments, the chemical analyses and physical properties of the leathers are given fully. The four types of leather so produced were similar. The small differencs between them suggest that there is no advantage in extending the total time in layers from 5 to 10 months if the mixed dust is used. There is a slight advantage in the longer time if pure oak bark is used. With oak bark only, prolonged layering suprisingly gave a more mellow leather of greater substance and lower resistance to water penetration. R.H.T.

Report of the French Hide Powder Commission. By G. Parsy. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 113 (1951). American #25 and French EFT5 Hide Powders were compared, as well as the corresponding kaolins. A table is given showing the average results of the committee work. EFT5 Hide Powder is the more uniformly white and is woolier. The American kaolin is very white and fine, and gives a somewhat higher blank, possibly because it passes the Durieux Super filter paper more easily. Several workers noted that it filtered more rapidly. It is concluded that, although the American Hide Powder is not as attractive as the EFT5, it gives practically identical results on standard extracts and can be used interchangeably, and has been approved as such. The Commission's ideas on the international admission are set forth: (1) Sampling: to be done by one member delegated by the Commission; with costs of packing, shipping, customs, etc., to be paid

by the Union. (2) Moisture: to be between 10 and 13 per cent. (3) Mineral Matter: maximum, 0.2 per cent of the anhydrous powder. (4) Matter not obsorbable by 1 g. kaolin: maximum, 1.2 per cent dry basis. (5) Blanks: (a) Distilled Water: maximum, 0.001 g. residue from 50 ml. after filtering. (b) Distilled Water plus 1 g. kaolin: maximum, 0.0015 g. residue from 50 ml. of filtrate. (c) Hide Powder with distilled water, then 1 g. kaolin and filtered: maximum 0.004 g. per 6.25 g. anhydrous powder, at 18-20°C. (6) pH: 6.25 g. anhydrous powder in equilibrium (24 hrs. at 18-20°C) with 100 ml. of *N* 10 KCl of pH 5.5, in a porcelain or fused silica container, and decanted, the pH to be between 5.0 and 5.8. (7) Detannisation: when tested against standard extracts, the nontannins shall differ by not more than $\pm$ 0.2 from those obtained with the last two previous official hide powders. (8) Examination Delay: when a lot of powder is ready, it is to be inspected and sampled by the appointees, and shipped to the members of the commission. The results shall be returned within 1 month. It is suggested that the Commission be made up of 3 Tanners, 3 Extract Manufacturers, and 3 Independents. A.N.K.

The Astringency of Vegetable and Chrome Tanning Liquors. By Ch. Gastellu. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 117. (1951). The importance of astringency is indicated, and its manifestations discussed. In *Vegetable Liquors,* the factors affecting astringency are: (1) The nature of the material used: tannins being divided into Astringent and Non-Astringent. Whereas the latter penetrate quickly, give a soft leather permeable to water, and low yield, the former penetrate slowly, give firm leather resistant to water, and high yield. For proper tannage, especially in the case of rapid processes, the hide must first be penetrated completely in non-astringent liquors and then gain the required firmness, etc., by use of more astringent liquors later. Prior to 1939, sulfited quebracho was the main non-astringent and chestnut the main astringent materials. Just as the astringent ordinary quebracho can be made non-astringent by chemical means, chestnut can be "sweetened"; on the other hand, the non-astringent wattle can be treated to behave astringently. (2) the Acidity of the liquor is next most important. The optimum pH for hide-tannin fixation is in the range of 3 to 3.5 and the astringency is then a maximum. By starting the tannage at pH, say, 5.5 and gradually lowering to pH 4 or 3.5 as the tannin penetrates, restricted penetration and harsh grain are avoided. Acidity is not only a matter of pH but of the type of acid present, the weaker acids having a greater effect on astringency (at a given pH) than have the strong acids. Titratable acidity is therefore important. (3) The ration of Tans/Nontans is also important. In a suitably regulated yard for rapid tannage, the early liquors will have about 1 per cent tannin together with two to three times as much nontans; in the early liquors of a slow tannage, while the acidity is high the nontans are also high and the tannins very low, so that the liquors are non-astringent. (4) An increase in temperature increases speed of penetration and the fixation and, carefully done, leads to thick, firm, leather of high degree of tannage. (5) Concentration, by affecting the particle size of the tannin, plays a part. In *Chrome Liquors,* astringency is also important. (1) Basicity; the more basic the liquor, the more rapidly and completely is the chrome fixed, while the rate of penetration is correspondingly reduced. As basicity is increased, the size of the particles increases by polymerisation, which increases the astringency. These two effects are concurrent and result in increased degree of olation, which causes a further increase in the astringency. Hence, for a proper measure of the astringent properties of a liquor, not only the basicity but also the Flocculation Index (Meunier) and the Degree of Olation must be determined. (2) Neutral Salts act to reduce the astringency. However, the salts of organic acids have a masking action which increases their effect and results in more uniform penetration and a finer grain, with less chrome fixed. A.N.K.

Glues and their Use in the Shoe Industry. By M. Giroflier. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 131 (1951). The different types of glues and cements are discussed: (1) Latex Base. A description of the Hevea tree and the methods of obtaining and stabilising the latex are given. Latex glues are not pure latex but contain added casein dissolved in ammonia, or emulsions of resins with a rubber solvent. These additives increase the adhesion and lower the viscosity. Where self-vulcanising glues are needed, suitable additions are made. Usual latex concentrations range from 30-60 per cent. (2) Crepe or Smoked Leaf base: Crepe is obtained by acidic coagulation of latex; smoked leaf is made by coagulating the latex, washing the coagulum, rolling into thin sheets, and submitting it to action of smoke until suitably dried. For cements, these materials are dissolved in organic solvents. For reasons of health, dichlorethane; trichlorethylene and naphthas are preferred to the aromatics. A typical cement is made by kneading the crepe with 8-10 per cent of naphtha and 4-6 per cent of trichlorethylene. Usually 10-40 per cent of rosin or of rosin esters are added. (3) Synthetic Rubber based: Synthetic rubbers are firmer, less elastic, and more wear-resisting than crepe. The molecular structure is more three-dimensional, so that they have a lower solubility in rubber solvents. To increase solubility, they are kneaded, dry, on calendars, with materials such as ZnO, to break down some of the structure, when the material becomes as soluble as crepe in the usual solvents, and is also soluble in certain ketones, which permits of quicker drying. Such solutions are not very stable with time but the addition of suitable antioxidants has overcome this. (4) Cellulose Glues. are based on nitrocellulose or cellulose acetate, which are only soluble in certain organic solvents. Suitable plasticisers are required. Such cements contain 16-25 per cent of cellulose ester and 5-15 per cent of plasticiser. An Italian invention ("Ago") adds 1-2 per cent of oxalic, tartaric or citric acid to lower the viscosity and permit a higher solids content. (5) Vegetable glues: are little used, but a list is given. (6) New Types of Cement: (a) Vinyl acetate is soluble in the usual cellulose solvents, giving solutions of low viscosity, thereby permitting higher solids content. (b) Glues based on Chlorinated Vinyl Chloride while the material is very insoluble, increased degree of chlorination makes for solubility in the usual solvents, giving great fluidity and good cementing powers. *Properties of Different Glues*: strength is not the only requirement, viscosity, wetting power, affinity for and penetration into the substrate being equally important, and the glues mentioned above are listed in decreasing order for each of these properties. *Utilisation in the Shoe Factory*: (1) GOODYEAR: *Upper Folding;* either latex or crepe. *First Lining;* latex best, then crepe. *Facing,* use a mixture of cork and heavily plasticised cellulose. *Attaching;* usually crepe, but latex also suitable. *Cementing the Channel;* (sole leather; latex or neoprene. *Cementing the Sole and Heel;* preferably latex. (2) *MIXED WELT*: this process is similar to the Goodyear but often used with leather substitutes. The insole can be of synderm as well as the welt, the mid-sole is of rubber, the out-sole of vulcanized rubber or any composition. In such cases, latex is eliminated. The facing can be of crepe glue and cork; the attaching is with crepe; cementing the channel (rubber or neo-composition sole) with a neoprene glue. (3) *WELDED PROCESS*: mostly used for women's shoes, the uppers being cemented directly to the insole with either a cellulose or, preferably, latex cement. For cementing the outsole, neoprenes are replacing the celluloses as they adhere better, dry more rapidly, and tie up the presses less. In Louis XV manufacture, the breast of the heel can be cemented with latex, crepe or, best, neoprene cement. (4) *SLIP-LASTING PROCESS*: the glue varies with the mid-sole used: with pressed felt, latex penetrates both the felt and the leather wrapper; with a cork/rubber mixture, latex is necessary for the wrapper and crepe for the sole. For the outsole, which may be of leather, crepe, rubber or composition, a neoprene cement is needed. Attempts are being made to cement the outsole of Goodyear-type shoes to avoid channelling, sole-wetting, channel cementing, and wet-rolling which cause stains; thereby a better wearing shoe would be obtained since there would be

no outsole threads to break when the lips of the channel wear. *Storage of Glues*: Latex-type; are most sensitive as liable to irreversible gelling. They should be stored in a cellar with only small temperature changes, and then for no more than 2-3 months, with the containers hermetically sealed. Solution and Neoprene type: are less sensitive but require similar conditions but may be stored for 5-6 months. Cellulose and Polyvinyl cments are quite stable and may be stored in sheds as long as they are kept tightly sealed to avoid evaporation loss.
A.N.K.

Antiseptics and Germicides in the Leather Industry. By U. J. Thuau. ***Rev. Tech.*** *Inds. Cuir.* **43,** 105 (1951). Fourth of a series (see Abstracts, *This Journal*, **49,** 523 & 527 (1954), et seq.,) The preparation and properties of salicylic and benzoic acids, and of formaldehyde and trioxymethylene are described. Salicylic acid is a more powerful disinfectant than phenol, while benzoic acid is more powerful still. Formaldehyde and trioxymethylene are very powerful but cannot be used with untanned stock, being tanning agents. They are also used in the production of syntans. The manufacture of both natural and synthetic camphor is described and it has both antiseptic and medicinal uses. Of the essential oils, those of wintergreen, birch, sassafras and aniseed are mentioned; these are used both for their odor and antiseptic properties. Birch oil is a good insecticide. α and β naphthol, their sodium salts, and naphthalene are derived from coal tar and are described. Naphthalene is both an antiseptic and antiparasite: the naphthols are the better disinfectants, α being the better, though more costly. Their sodium salts are more soluble in water but not as effective. On raw hides and skins, they are effective against bacteria, parasites and insects but cause difficulty in unhairing and dyeing so are really only of value in the case of fur skins. (To be continued). A.N.K.

The Synthetic and Protein Fibers. *Rev. Tech. Inds. Cuir.* **43,** 109 (1951). A reprint of an article published by "Les Informations Industrielles et Commerciales" under the title of "Original Techniques and New Products in France and Abroad". Due to the scarcity and high cost of natural fibers, many artificial and synthetic fibers have been prepared and are being produced on an increasing scale. The article discusses the preparation and properties of most of the more important produced in France, Switzerland, Britain, Russia, and America, and a table is given summarizing these. A.N.K.

Air Conditioning and Climatisation and their Industrial Applications. *Rev. Tech. Inds. Cuir.* **43,** 114 (1951). A precis of an article from the first three 1951 issues of "Technique Suisse". While temperature and humidity control are of the utmost importance in the textile industry, many other industries have a similar need. In the leather industry, heating in winter requires additional moisture to prevent the stock from drying out while, in summer, cooling is needed for proper working conditions. By the use of a thermal pump, heating in winter and cooling in summer can be obtained with the same equipment. Mention is made of some needs of the food industry, including abattoirs.
A.N.K.

Mechanical Scudding and Scouring. *Rev. Tech. Inds. Cuir.* **43,** 115 (1951). The purposes of scudding are detailed, and it is indicated that the skin must be so supported that the pores are opened, thereby facilitating removal of epidermal debris. The usual "beam" has the correct shape, and the operator can adjust the pressure applied to suit the particular part of the hide being worked. The usual machine (Leidgen?) has a rubber apron which takes a concave shape and so tends to close the pores and requires a great deal more pressure. Other machines are constructed like a fleshing machine but,

while the pores are opened, the pressure is constant and cannot readily be changed from skin to skin. The "Alisora" (Badische Maschinenfabrift, Durlach) is built like a drum setting-out machine: due to the elastic nature of the bloster, which compensates for variations in thickness, and to the wide range of pedal-applied pressure, which enables the pressure to be adjusted to suit the part of the hide being worked, this machine gives much the same action as hand-scudding. By careful design, the machines occupies 30 per cent less space than previous equipment, and the drum can be stopped or reversed at any point. This machine offers the tanner the possibility of improved quality, elimination of hand-work, and lower cost. A.N.K.

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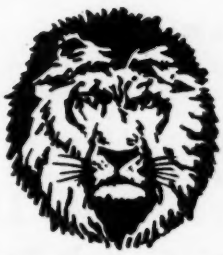

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INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY, Dyestuff Department XVII
AMERICAN CYANAMID COMPANY, Leather Chemicals Department V
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXXVI
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XIV
BARIUM REDUCTION CORPORATION XXV
BARKEY IMPORTING CO., INC. XXXIV
BONA ALLEN, INC. XXXIII
BUCKMAN LABORATORIES, INC. XV
BUFFALO EXTRACT & SUPPLY CO. XLII
CHEMTAN COMPANY XXI
DIAMOND ALKALI CO. XL
E. I. DuPONT DeNEMOURS & CO. XXXIX
EISENDRATH TANNING CO. XXVII
EUROPEAN CHESTNUT MFG'S ASSO. XIX
FRANK F. MARSHALL ..... XXXI— XLII
GARDEN STATE TANNING INC. XXXI
GEIGY COMPANY, INC. XXXVII
GENERAL DYESTUFF COMPANY ..... VIII—IX
HOOKER ELECTROCHEMICAL CO. XVI
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. X
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. XXXVIII
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE XI
MUTUAL CHEMICAL CO. OF AMERICA XXXV
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XII
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XVIII
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XIII
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLIV—Inside Back Cover
TANIMEX CORPORATION XLI
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXI—XLII
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXXVI
UNITED STATES TESTING COMPANY XXXV
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XX

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